Environment Canada
Environmental Protection Service

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ENVIRO

Technical

Information for

Problem

Spills

CARBON DIOXIDE

November 1984

Canada

85-4290/

ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS MANUALS

Environmental and Technical Information for Problem Spills (EnviroTIPS) manuals provide detailed information on chemical substances. This information is intended to assist the reader in designing countermeasures for spills and to assess their impact on the environment. The manual has been reviewed by the Technical Services Branch, Environmental Protection Service, and approved for publication. Approval does not necessarily signify that the contents reflect the views and policies of the Environmental Protection Service. Mention of trade names or commercial products does not constitute endorsement for use.

EnviroTIPS manuals are available from

Publications Section
Environmental Protection Service
Environment Canada
Ottawa, Ontario
CANADA
K1A 1C8

CARBON DIOXIDE

ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS

Technical Services Branch
Environmental Protection Programs Directorate
Environmental Protection Service
Ottawa, Ontario

November 1984

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Cat. No. En 48-10/24-1984E
ISBN 0-662-13649-7
BEAUREGARD PRESS LIMITED

FOREWORD

The Environmental and Technical Information for Problem Spills (EnviroTIPS) manuals were initiated in 1981 to provide comprehensive information on chemicals that are spilled frequently in Canada. The manuals are intended to be used by spill specialists for designing countermeasures for spills and to assess their effects on the environment. The major focus of EnviroTIPS manuals is environmental. The manuals are not intended to be used by first-response personnel because of the length and technical content; a number of manuals intended for first-response use are available. The information presented in this manual was largely obtained from literature review. Efforts were made, both in compilation and in review, to ensure that the information is as correct as possible. Publication of these data does not signify that they are recommended by the Government of Canada, nor by any other group.

ACKNOWLEDGEMENTS

The final version of this manual was prepared by the staff of the Environmental Protection Service who wrote extensive revisions to the text, drafted illustrations and incorporated all comments and additions.

The level of detail present was made possible by the many individuals, organizations and associations who provided technical data and comments throughout the compilation and subsequent review. The draft of this manual was prepared under contract to Environment Canada by M.M. Dillon Consulting Engineers and Planners, Concord Scientific Corporation, and Waterloo Engineering Limited.

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1 SUMMARY

CARBON DIOXIDE (CO_2)

Colourless, odourless gas or liquid, or white solid

SYNONYMS

Dry Ice, Carbonic Anhydride, Carbonic Acid Gas, Carbonice, Anhydride Carbonique (Fr.), Liquefied Carbon Dioxide

IDENTIFICATION NUMBERS

UN No. 1845 (solid), 2187 (liquid), 1013 (gas); CAS No. 124-38-9; STCC No. 4904509 (liquefied)

GRADES & PURITIES

Available in various grades, usually of 99 percent purity. Available as solid (dry ice), liquid, or gas

IMMEDIATE CONCERNS

Fire: Not combustible. Frequently used as a fire-fighting agent

Human Health: Low toxicity by all routes

Environment: Harmful to some freshwater aquatic species in concentrations of 20 mg/L or less

PHYSICAL PROPERTY DATA

Shipping state: liquid (liquefied compressed gas), gas, solid
State (15°C, 1 atm): gas
Boiling Point: sublimes at -78.5°C
Flammability: not combustible
Vapour Pressure: 5778 kPa (21°C)
Specific Gravity (water = 1): 1.1 (-37°C) liquid
Specific Gravity (air = 1): 1.5 (25°C) gas
Solubility (in water): 0.145 g/100 mL (25°C)
Odour Threshold: odourless

ENVIRONMENTAL CONCERNS

Levels of carbon dioxide just above the normal ambient level in the air are harmless to plant and animal species. Low levels (as low as 20 mg/L) of CO_2 in water are harmful to freshwater species.

HUMAN HEALTH

TLV•: 5000 ppm (9000 mg/m^3)
IDLH: 50 000 ppm

Exposure Effects

Inhalation: Inhalation of heavy vapour concentrations may cause headache, dizziness, shortness of breath, muscular weakness, drowsiness, and ringing in ears. Concentrations of over 20 to 30 percent can result in unconsciousness and death

Contact: Contact with liquid or solid can produce frostbite

IMMEDIATE ACTION

Spill Control

Restrict access to spill site. Notify suppliers. Avoid contact with liquid and solid, and inhalation of vapour. Keep contaminated water from entering sewers or watercourses.

2 PHYSICAL AND CHEMICAL DATA

Physical State Properties

Appearance	Colourless gas (HCG 1981) Liquid CO_2 is colourless; solid is white
Usual shipping state(s)	Liquid: liquefied gas (HCG 1981) Solid: dry ice
Physical state at 15°C, 1 atm	Gas
Melting point	Solid will sublime before melting at atmospheric pressure
Sublimation point	-78.5°C (HCG 1981; Kirk-Othmer 1978)
Triple point	-56.57°C at 518 kPa (Ullmann 1975; Matheson 1980)
Vapour pressure	5778 kPa (21°C) (HCG 1981)

Densities

Density	Gas: 1.977 g/L (0°C) (Ullmann 1975; Matheson 1980) Liquid: 0.759 g/mL (25°C) (Kirk-Othmer 1978)
Specific gravity	Liquid: 1.101 (liquid -37°C) (CRC 1980) Gas: 1.522 (21°C) (HCG 1981) (air = 1), 1.53 (0°C) (Matheson 1980)

Fire Properties

Flammability	Nonflammable, will not burn (HCG 1981)
Decomposition	At high temperatures (above 1700°C), begins to decompose to CO. Decomposition is 15.8 percent at 2227°C (Kirk-Othmer 1978)

Other Properties

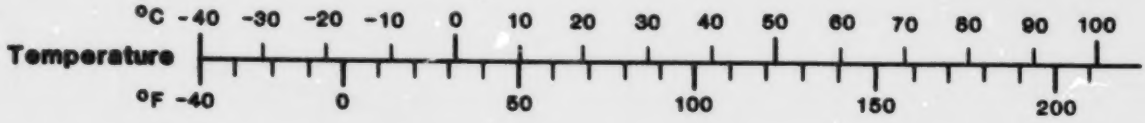
Molecular weight of pure substance	44.01 (CRC 1980)
Constituent components of typical commercial grade	99.5 percent and higher CO_2 (HCG 1981)
Refractive index	1.000448 to 1.000454 (0°C) (Matheson 1974)
Viscosity	Gas: 0.015 mPa•s (25°C) (Kirk-Othmer 1978) Liquid: 0.070 mPa•s (20°C) (Ullmann 1975)
Liquid interfacial tension with air	1.16 mN/m (liquid, 20°C) (CRC 1980)
Liquid interfacial tension with CO_2 gas	9.1 mN/m (-25°C) (CRC 1980)
Latent heat of fusion	7.95 kJ/mole (-57°C) (Matheson 1974)

Latent heat of vaporization	15.3 kJ/mole (-56.5°C) (Kirk-Othmer 1978)
Latent heat of sublimation	25.1 kJ/mole (-78.5°C) (HCG 1981)
Heat of formation	-393.5 kJ/mole (25°C) (JANAF 1971)
Entropy	213 J/(mole•K) (Ullmann 1975)
Ionization potential	13.77 eV (Rosenstock 1977)
Ionization constant (in water)	first: 3.5×10^{-7} (18°C) second: 4.4×10^{-11} (25°C) (Kirk-Othmer 1978)
Heat capacity (gas)	
Constant pressure (C_p)	37.564 J/(mole•°C) (25°C) (Matheson 1980)
Constant volume (C_v)	28.541 J/(mole•°C) (20°C) (Matheson 1980)
Specific heat ratio (γ) (C_p/C_v)	1.316 (Matheson 1980)
Critical pressure	7382 kPa (HCG 1981; Matheson 1980)
Critical temperature	31.1°C (HCG 1981; Kirk-Othmer 1980)
Coefficient of thermal expansion	3.71×10^{-3}/°C (20°C) (Perry 1973)
Thermal conductivity	1.64×10^{-4} W cm^{-1} K^{-1} (25°C) (Ullmann 1975)
Saturation concentration (calc.)	9482 g/m^3 (15°C) (CRC 1980)
Diffusivity	0.138 cm^2/s (0°C) (in air) (Perry 1973) 1.96×10^{-5} cm^2/s (in water, 25°C) (Perry 1973)
pH of aqueous solution	3.7 (HCG 1981)
Solubility	
In water	0.348 g/100 mL (0°C), 0.145 g/100 mL (25°C) (CRC 1980), 0.058 g/100 mL (60°C)
In other common materials	Soluble in most liquids (Linke 1958): Solubility is given for some common solvents, in cm^3 CO_2/g solvent (Ullmann 1975) (all are at 10°C): Acetone, 10.5; Benzene, 2.9; Diethyl ether, 7.8; Ethanol, 4.3; Methanol, 5.0; Toluene, 3.4
Vapour Weight-to-Volume Conversion Factor	1 ppm = 1.829 mg/m^3 (20°C) (Verschueren 1977)

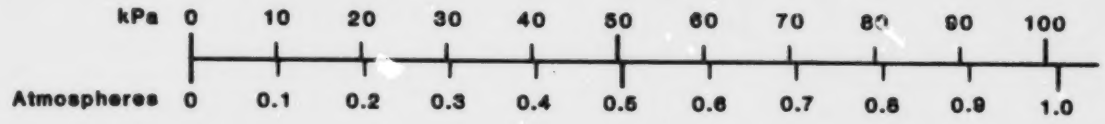
TABLE 1

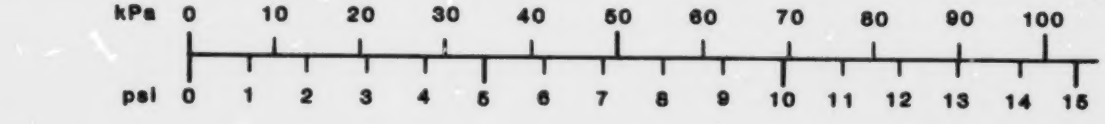
CARBON DIOXIDE

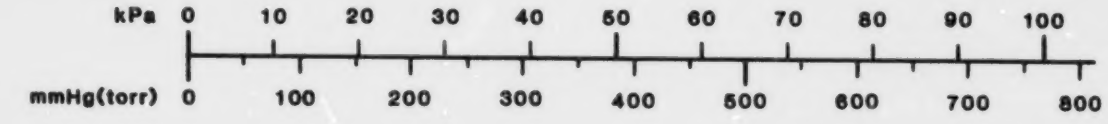
CONVERSION NOMOGRAMS



Pressure 1 kPa = 1 000 Pa







Viscosity

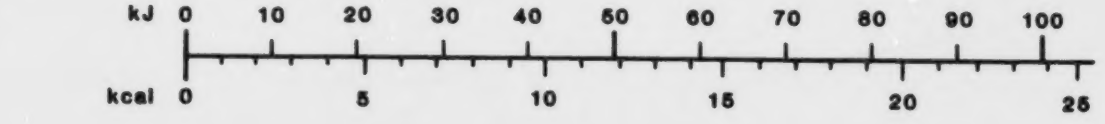
Dynamic 1 Pa·s = 1 000 centipoise (cP)

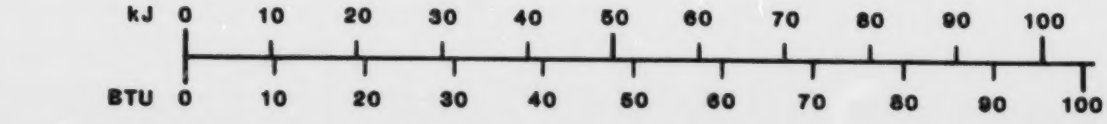
Kinematic 1 m^2/s = 1 000 000 centistokes (cSt)

Concentration (in water)

1 ppm ≅ 1 mg/L

Energy (heat) 1 kJ = 1 000 J





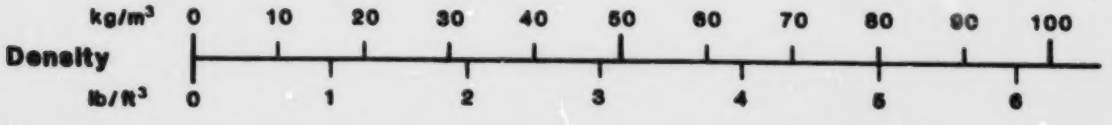


FIGURE 1

CARBON DIOXIDE

VAPOUR PRESSURE VS TEMPERATURE

Reference: HCG 1981

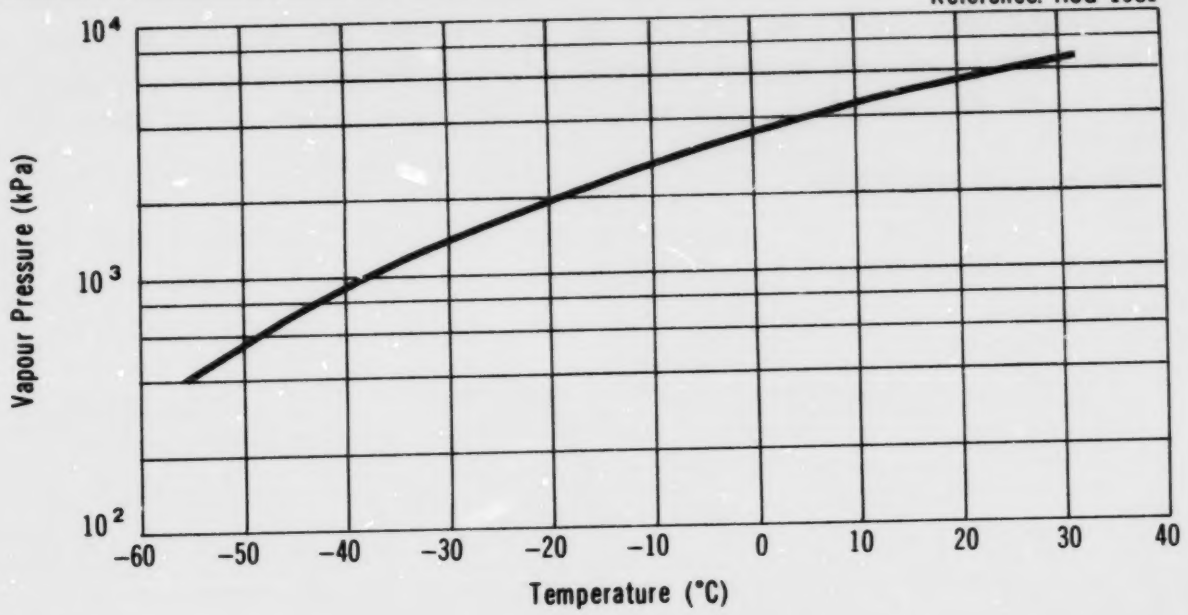


FIGURE 2

CARBON DIOXIDE

LIQUID DENSITY vs TEMPERATURE

Reference: HCG 1981

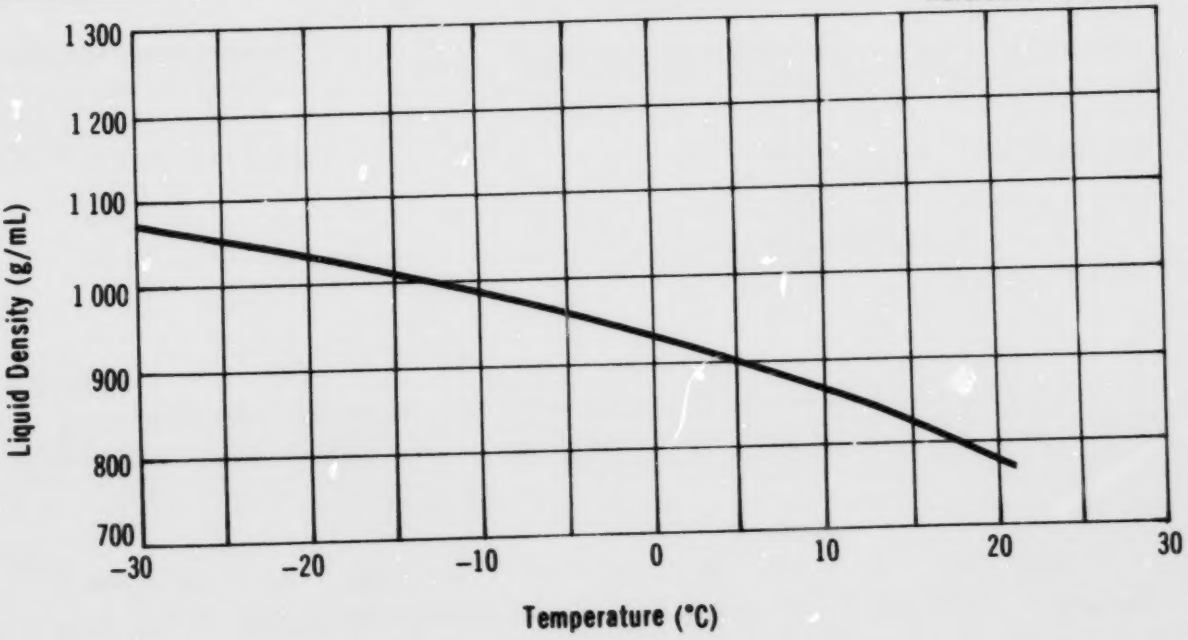


FIGURE 3

CARBON DIOXIDE

GAS DENSITY

Reference: MATHESON 1980

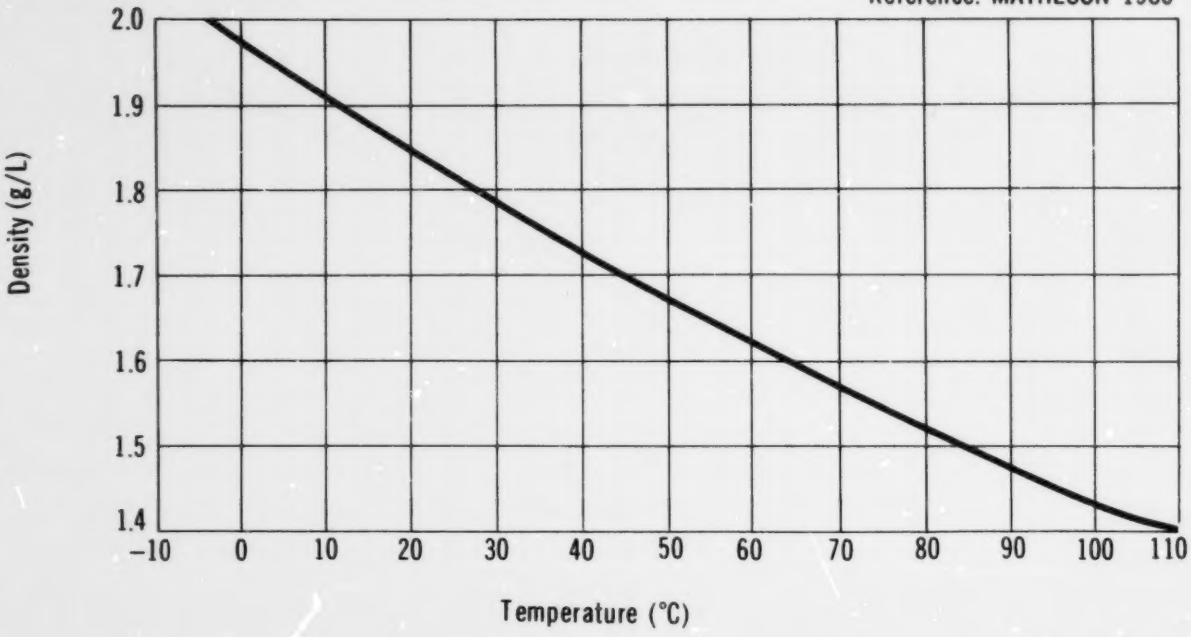


FIGURE 4

CARBON DIOXIDE

LIQUID VISCOSITY vs TEMPERATURE

Reference: Chem. Eng. 1974

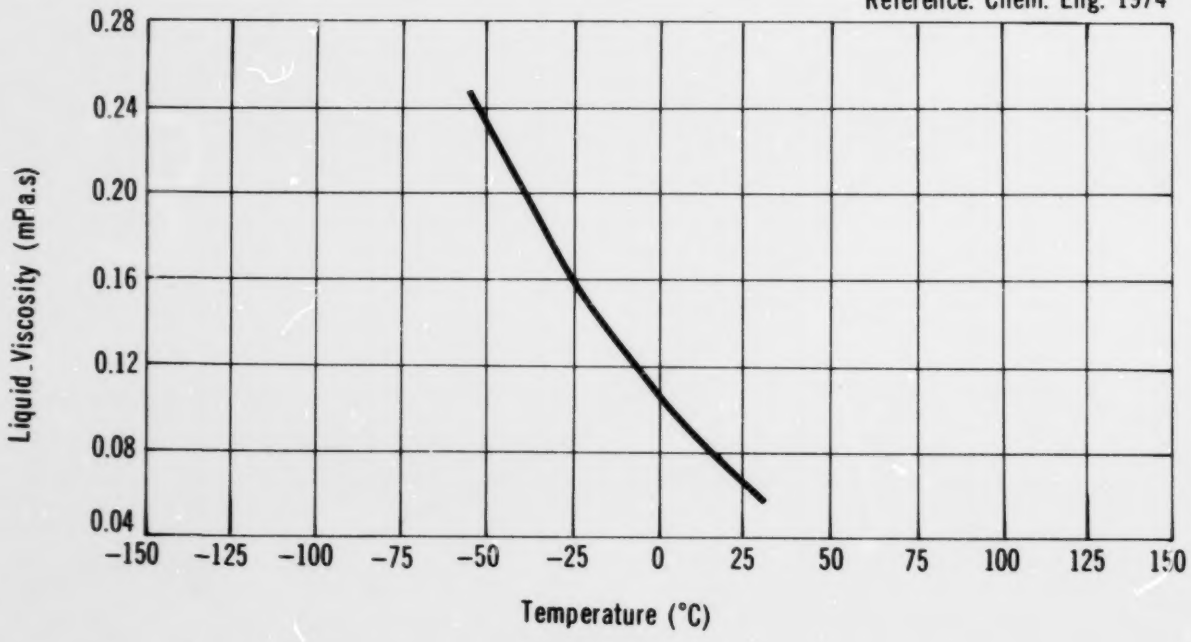


FIGURE 5

CARBON DIOXIDE

VAPOUR VISCOSITY vs TEMPERATURE

Reference: Chem. Eng. 1974

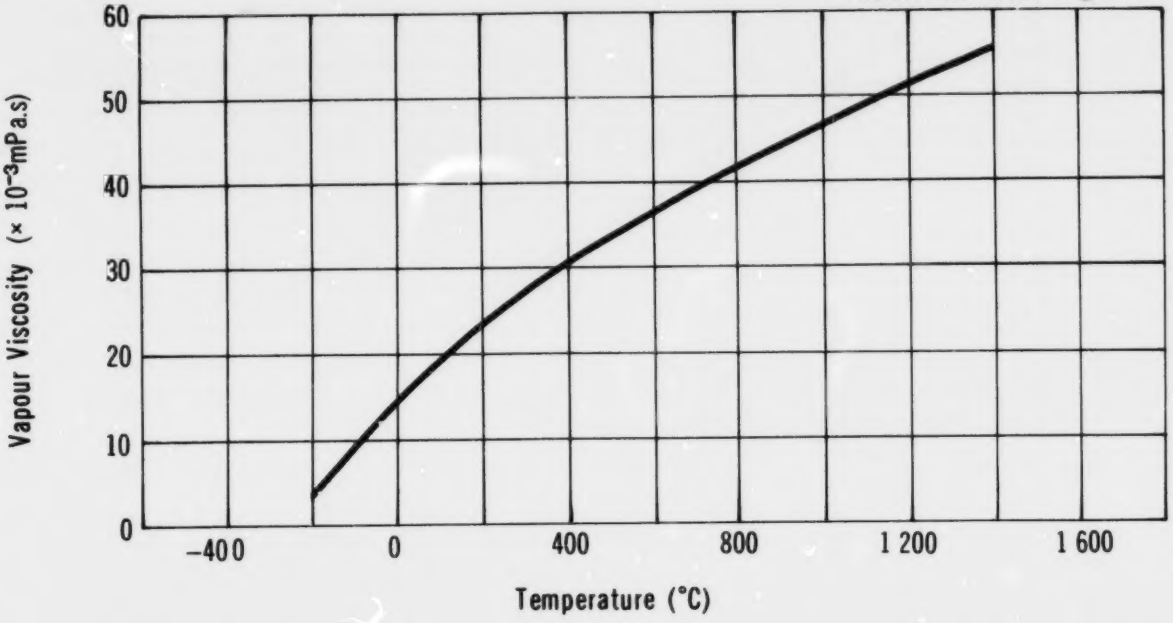


FIGURE 6

CARBON DIOXIDE

SOLUBILITY IN WATER vs TEMPERATURE

Reference: LINKE 1958

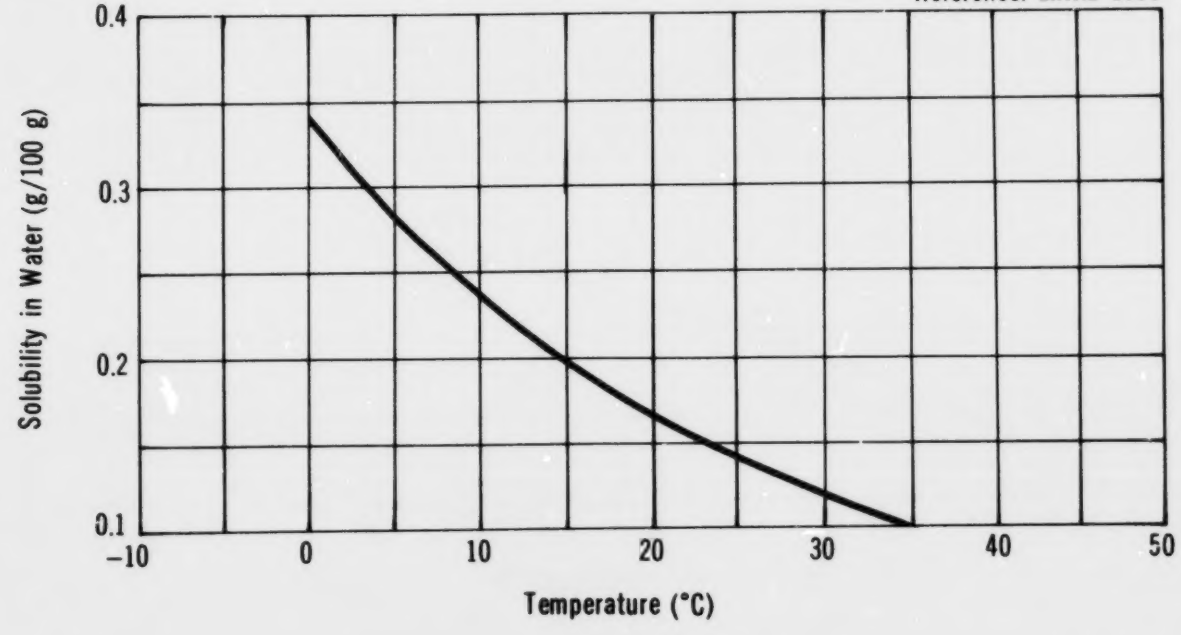
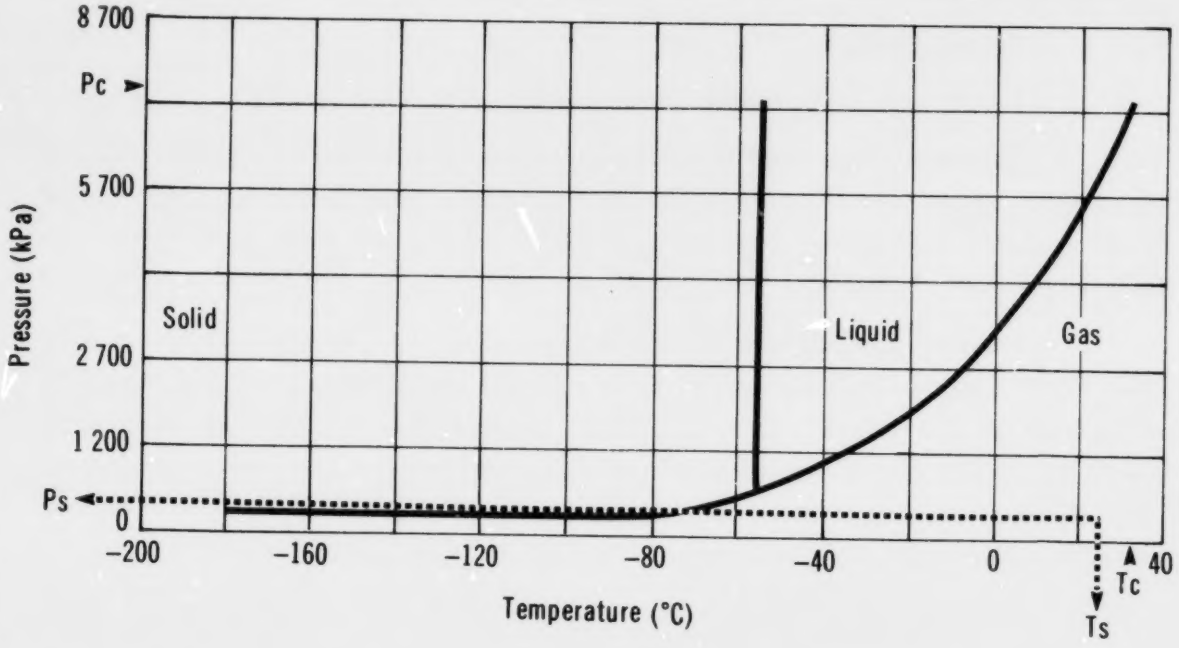


FIGURE 7

CARBON DIOXIDE

PHASE DIAGRAM



3 COMMERCE AND PRODUCTION

3.1 Grades, Purities

Carbon dioxide is available in three states: liquid, gas or solid.

3.1.1 Carbon Dioxide, Solid (Air Products SGDS 1981; Liquid Carbonic 1975). Dry ice of purities of 99 percent or less is commonly available. Solid carbon dioxide or dry ice is also available in a research grade (large blocks or pellets) at a purity of 99.995 percent (at a temperature of -78.4°C).

3.1.2 Liquid Carbon Dioxide (Canadian Liquid Gas TDS 1981; Air Products SGDS 1981; Liquid Carbonic 1975). Liquefied carbon dioxide with purities of around 99 percent is available for bulk shipment by truck or rail. Liquid carbon dioxide is also available as a bulk liquid in standard refrigeration recovery systems, operating at a pressure of 2070 kPa, at -17.8°C. A Compressed Gas Association grade or Coleman grade is available with a purity of 99.99 percent.

3.1.3 Gaseous Carbon Dioxide (Air Products SGDS 1981; Liquid Carbonic 1975). Gaseous carbon dioxide is available in standard high pressure cylinders, at a pressure of 5826 kPa at 21°C. Industrial, medical and commercial (C.P.) grades are available with a minimum purity of 99.5 percent.

3.2 Domestic Manufacturers (Corpus 1983; CBG 1980; CCPA 1981, 1982; CCR 1978; Scott 1979)

These are corporate headquarters' addresses and are not intended as spill response contacts.

Allied Canada Inc.
201 City Centre Drive
Mississauga, Ontario
L5B 2T4
(416) 276-9211

Canadian Fertilizers Ltd.
P.O. Box 1300
Medicine Hat, Alberta
T1A 7N1
(403) 527-8887

Canadian Industries Ltd.
90 Sheppard Avenue East
P.O. Box 200, Stn. A
Willowdale, Ontario
M2N 6H2
(416) 229-7000

Canadian Liquid Air Co. Ltd.
1155 Sherbrooke Street West
Montreal, Quebec
H3A 1H8
(514) 842-5431

Cominco Ltd.
200 Granville Street
Vancouver, British Columbia
V6C 2R2
(604) 683-0611

Lacan Carbon Dioxide Ltd.
Subsidiary of Canadian Liquid Air Ltd.
and Canadian Oxygen
850 Burlington Street East
P.O. Box 3002, Station B
Hamilton, Ontario
L8L 7Y1
(416) 547-1601

Liquid Carbonic Canada
1945 Graham Blvd.
Montreal, Quebec
H3R 1H1
(514) 731-6461

Nitrochem Inc.
2055 Peel Street, Suite 800
Montreal, Quebec
H3A 1V4
(514) 849-9222

Northern Breweries Ltd.
503 Bay Street, P.O. Box 280
Sault Ste. Marie, Ontario
P6A 5L9
(705) 254-7373

Sherritt Gordon Mines Ltd.
Box 28
Commerce Court West
Toronto, Ontario
M5L 1B1
(416) 363-9241

Simplot Chemical Co. Ltd.
P.O. Box 940
Brandon, Manitoba
R7A 6A1
(204) 728-5701

Union Carbide Canada Ltd.
123 Eglinton Avenue East
Toronto, Ontario
M4P 1J3
(416) 488-1444

3.3 Major Transportation Routes

Current Canadian production of carbon dioxide is located primarily in Alberta, at Medicine Hat, Calgary, Carseland and Fort Saskatchewan (58 percent of total production) and in Ontario, at Amherstburg, Courtright, Maitland and Niagara Falls (28 percent of total production). Other facilities are located in Quebec and Manitoba.

3.4 Production Levels (Corpus 1983)

Company, Plant Location	Nameplate Capacity kilotonnes/yr (1982)
Allied Canada Inc., Amherstburg, Ont.	220
Canadian Liquid Air, Calgary, Alta.	16
C-I-L, Courtright, Ont.	144
Canadian Fertilizers, Medicine Hat, Alta.	392
Cominco, Calgary, Carseland, Alta.	455
Lacan, Niagara Falls, Ont.	47.5
Liquid Carbonic Canada, Montreal, Que.	85
Liquid Carbonic Canada, Maitland, Ont.	57.5
Liquid Carbonic Canada, Courtright, Ont.	71.5
Liquid Carbonic Canada, Brandon, Man.	25
Liquid Carbonic Canada, Medicine Hat, Alta.	25.5
Liquid Carbonic Canada, Ft. Saskatchewan, Alta.	53
Nitrochem, Maitland, Ont.	40
Sherritt Gordon Mines, Ft. Saskatchewan, Alta.	72
Simplot Chemical, Brandon, Man.	128
Union Carbide Canada, Montreal East, Que.	58
TOTAL	1890
Domestic Production (1982)	1452.5
Imports (1982)	3
TOTAL SUPPLY	1455.5

3.5 Manufacture of Carbon Dioxide (Shreve 1977; Kirk-Othmer 1978)

3.5.1 General. Carbon dioxide is produced as a by-product from synthetic ammonia and hydrogen plants, from combustion processes, from fermentation, and from soda ash.

3.5.2 Raw Materials. By-product gases from combustion and chemical processes and from fermentation are the raw materials used in the manufacture of carbon dioxide.

3.5.3 Manufacturing Processes. Carbon dioxide off-gas is purified and concentrated by an absorption process. First, the process gas is water-scrubbed in columns to remove impurities; carbon dioxide is then removed by selective absorption. Absorbents used are: sodium and potassium carbonate and ethanolamine solutions. The absorbent is stripped of carbon dioxide by steam heating in a subsequent tower. The carbon dioxide evolved is cooled, scrubbed to remove residual sulphides and amines, compressed, cooled, and finally liquefied.

Fermentation processes produce by-product gas containing up to 99.5 percent carbon dioxide; concentration by absorption is thus not required. The gas is instead passed directly through scrubbing towers, which remove residual alcohol vapour, oxidize remaining organics with a chromate solution, and dehydrate the gas with sulphuric acid. The gas is then scrubbed to remove residual acid (with a carbonate solution) and odours (with glycerine) before being finally compressed and passed to storage.

3.6 Major Uses in Canada (Corpus 1983; Air Product SGDS 1981; Liquid Carbonic 1975)

Major uses are in urea, soda ash, and carbonated beverage production, in industrial inerting, and in oil-well servicing. In 1982, 73 percent of production in Canada was used for making urea, and 15 percent for the production of soda ash. The remainder is fairly evenly divided among the other uses.

3.6.1 Solid. The solid form, dry ice, is used extensively for refrigerating food, blending and pulverizing heat-sensitive materials in industrial processes, and controlling chemical reaction temperatures.

3.6.2 Liquid. Liquid carbon dioxide has widespread applications as a food refrigerant; as a refrigerant in railroad cars, ships, and trucks; and as a pressure source in coal blasting and gas-operated tools, etc.

3.6.3 Gas. Gaseous carbon dioxide is typically used in the processing and storage of perishable food as an inert atmosphere; as a carbonating agent in beverages; in welding as

a shielding medium; in aerosol dispensers as a propellant; in fire extinguishers; for irrigation; in the manufacture of aspirin; in the treatment of alkaline waste waters; and in the manufacture of foundry cores and molds.

3.7 Major Buyers in Canada (Corpus 1983; CBG 1980)

Alberta Gas Ethylene, Joffre, Alta.
BASF Canada, Laval, Que.; Cornwall, Ont.
Baldwin & Kroll, Edmonton, Alta.
Beta Well Service, Edmonton, Alta.
Borg-Warner, Calgary, Alta.
Budd Automotive, Kitchener, Ont.
Burns Foods, Calgary, Alta.
C-I-L, Edmonton, Alta.
C-I-L, Toronto, Ont.
Canada Dry, Toronto, Ont.
Canada Packers, Toronto, Ont.
Chubb Industries, Brampton, Ont.
Coca-Cola, Toronto, Ont.
Dominion Dairies, Toronto, Ont.
Dow Chemical Canada, Sarnia, Ont.; Fort Saskatchewan, Alta.
Dowell of Canada, Calgary, Alta.
Du Pont Canada, Maitland, Sarnia, Ont.
Esso Chemical Canada, Sarnia, Ont.
Ethyl Canada, Sarnia, Ont.
Firestone Canada, Hamilton, Ont.
Ford Motor, Windsor, Ont.
Glidden, Div. Sico, Toronto, Ont.
B.F. Goodrich Canada, Kitchener, Ont.
Goodyear Canada, Toronto, Ont.; Valleyfield, Que.
Halliburton Services, Calgary, Alta.
Hayes-Dana, Thorold, Ont.
International Paints, Montreal, Que.
Michelin Tire, Granton, N.S.
Monsanto Canada, Montreal, Que.
Nowsco Well Service, Calgary, Alta.
PPG Industries Canada, Toronto, Ont.
Pepsi-Cola, Toronto, Ont.
Petrosar, Corunna, Ont.
Polysar, Sarnia, Ont.
Schlumberger of Canada, Calgary, Alta.
Seven-Up Canada, Toronto, Ont.
Sherwin-Williams Canada, Montreal, Que.
Swift Canadian, Toronto, Ont.
Union Carbide Canada, Montreal, Que.
Uniroyal Canada, Kitchener, Ont.

4 MATERIAL HANDLING AND COMPATIBILITY

4.1 Containers and Transportation Vessels

4.1.1 General. Liquid carbon dioxide is usually transported in steel pressure vessels equipped with safety devices. The vessels may be independent cylinders, railway tank cars, or tank motor vehicles.

4.1.2 Cylinders and Packaging. Cylinders are of seamless steel construction with a net mass from 9 to 23 kg (4 to 7 lb.) (CSS). Cylinders must comply with CTC/DOT specifications 3AI800, 3AAI800, 3AAXI800 and 3EI800. Class 3A and 3AA cylinders having higher service pressures also may be used (HCG 1981). Each cylinder is equipped with a frangible disc safety device designed to blow out and release the contents if the internal pressure exceeds 19 300 kPa (2800 psi) (TDGC 1980). Each specification is described in Table 2. Cylinder usage for carbon dioxide liquid is generally limited to small volume demands (GPD). Figure 8 shows some typical cylinder configurations. Laboratory cylinders are equipped with fittings to accept a CGA320 regulator with a 0.825 in., 14 threads per inch, right hand external thread with a flat-face seal (Matheson 1980).

Dry ice or solid carbon dioxide blocks weighing 23 to 27 kg (50-60 lb.) are wrapped in heavy kraft paper bags. They are stored and shipped in insulated containers and storage boxes of varying sizes (HCG 1981).

TABLE 2 CYLINDER SPECIFICATIONS

CTC/DOT* Specification Number	Description
3AI800	Seamless steel cylinder. Maximum service pressure 12 400 kPa (1800 psi).
3AAI800	Seamless steel cylinder. Maximum service pressure 12 400 kPa (1800 psi). Steels definitely prescribed. Maximum carbon content 0.28%.
3AAX1800	Seamless steel cylinder. Maximum service pressure 12 400 kPa (1800 psi). Minimum water capacity 455 kg (1000 lb.)
3E1800	Seamless steel cylinder. Maximum service pressure 12 400 kPa (1800 psi). Maximum diameter: 51 mm (2 in.) Maximum length: 610 mm (24 in.)

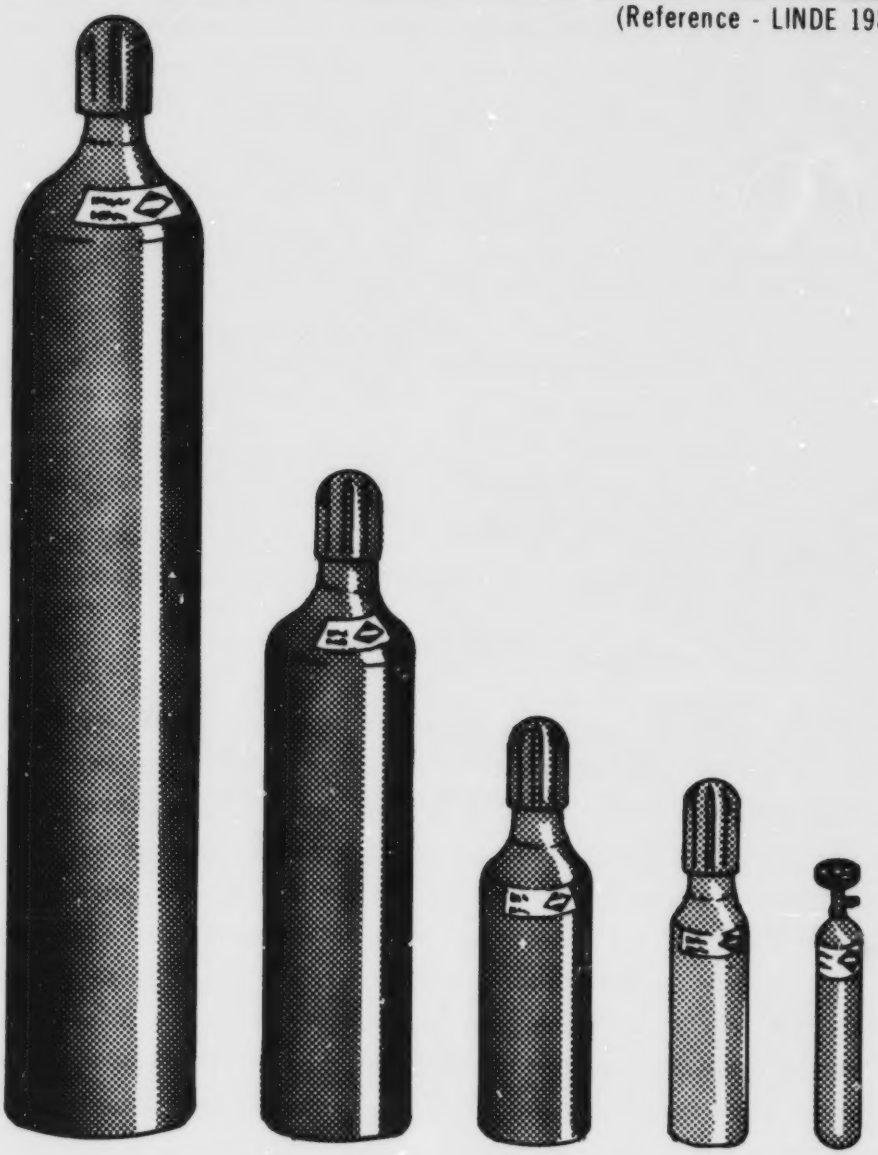
* Canadian Transport Commission and Department of Transportation (U.S.)

FIGURE 8

CARBON DIOXIDE

COMMON GAS CYLINDERS

(Reference - LINDE 1981)



Industry designation		**K**	**Q**	**G**	**F**	**LB**
Approx. size	**(mm)**	**229×1320**	**178×787**	**152×508**	**102×432**	**51×330**
	(in)	**9×52**	**7×31**	**6×20**	**4×17**	**2×13**
Approx. weight (empty)	**(kg)**	**60**	**29**	**13**	**5**	**1**
	(lb)	**132**	**65**	**29**	**10**	**4**

4.1.3 Railway Tank Cars. Railway tank cars used to transport liquefied carbon dioxide are described in Table 3 (RTDCR 1974). A railway tank car is illustrated in Figure 9; Table 4 indicates railway tank car details associated with this drawing.

TABLE 3 RAILWAY TANK CAR SPECIFICATIONS

CTC/DOT* Specification Number	Description
105A500W	Steel fusion-welded tank with manway nozzle. Insulated. Top unloading arrangement required. Maximum operating pressure 3450 kPa (500 psi). Bottom outlet or washout prohibited.
105A600W	Same as 105A500W except maximum operating pressure 4140 kPa (600 psi).

* Canadian Transport Commission and Department of Transportation (U.S.)

The only opening permitted in the tank is a single manway located in the centre at the top. Seven valves are mounted inside the dome cover; four of these are angle valves and the others are a safety relief valve and two pressure regulating valves. The safety relief valve must be set to open at a pressure not exceeding 3/4 of the test pressure of the tank. Two of the angle valves are for unloading liquid carbon dioxide while the other two are connected to the vapour space. Under each liquid valve is an eduction pipe fastened to the manway cover and extending to the bottom of the tank. At the top of each eduction pipe, immediately below the manway cover, is a rising-ball, excess-flow valve designed to close when the rate of flow of liquid carbon dioxide exceeds about 3180 kg/h (7000 lb./h). This is a protective device designed to close automatically against the flow of liquid carbon dioxide if the angle valve is broken off or, under certain conditions, if the unloading line is severed (TCM 1979).

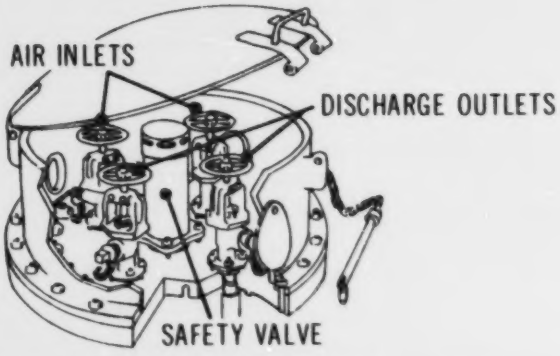
4.1.4 Tank Motor Vehicles. Carbon dioxide tank motor vehicles consist of a cargo tank pulled by a tractor. The maximum tank capacity is restricted by highway load limits. They must comply with Transport Canada Specifications TC331 or MC331 as outlined in Table 5 (HCG 1981). The capacities of highway tankers vary depending on the user requirements. All tanks are provided with heavy insulation (CD 1975). The only tank

FIGURE 9

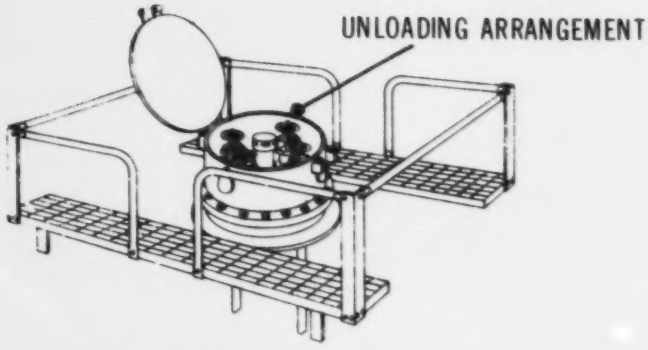
CARBON DIOXIDE

RAILWAY TANK CAR - CLASS 105A500W

Reference: TCM 1979; RTDCR 1974



Detail of top unloading arrangement



Detail of loading platform

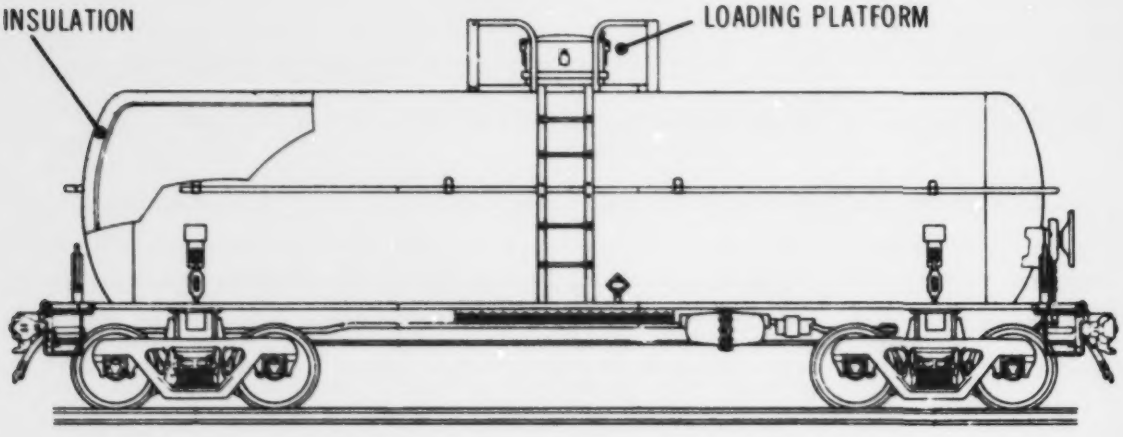


Illustration of tank car layout

TABLE 4 TYPICAL RAILWAY TANK CAR SPECIFICATIONS - CLASS 105A500W (TCM 1979; RTDCR 1974)

Description	Tank Car Size (Imp. Gal.) 8800 (55 ton)	15 000 (90 ton)
Overall		
Nominal capacity	40 000 L (8800 gal.)	68 000 L (15 000 gal.)
Car weight - empty	33 800 kg (74 600 lb.)	37 400 kg (82 500 lb.)
Car weight - (max.)	99 800 kg (220 000 lb.)	106 400 kg (263 000 lb.)
Tank		
Material	Steel	Steel
Thickness	17-24 mm (11/16-15/16 in.)	17-24 mm (11/16-15/16 in.)
Inside diameter	2.2 m (88 in.)	2.6 m (102 in.)
Test pressure	3450 kPa (500 psi)	3450 kPa (500 psi)
Burst pressure	8620 kPa (1250 psi)	8620 kPa (1250 psi)
Approximate Dimensions		
Coupled length	13 m (41 ft.)	15 m (48 ft.)
Length over strikers	12 m (39 ft.)	14 m (46 ft.)
Length of truck centres	9 m (28 ft.)	11 m (35 ft.)
Height to top of grating	4 m (12 ft.)	4 m (12 ft.)
Overall height	5 m (15 ft.)	5 m (15 ft.)
Overall width	3.2 m (127 in.)	3.2 m (127 in.)
Length of grating	2-3 m (7-10 ft.)	2-3 m (7-10 ft.)
Width of grating	1.5-2 m (5-6 ft.)	1.5-2 m (5-6 ft.)
Loading/Unloading Fixtures		
Unloading connection	51 mm (2 in.) via valve and 76 mm (3 in.) check valve; 6 mm (1/4 in.) outlet	
Valving	51 mm (2 in.) valve to vapour space	
Gauging Device	Float-type gauging device and thermometer well	
Safety Devices	Safety relief valve set at 2590 kPa (375 psi)	
Insulation	51-152 mm (2-6 in.) fibreglass insulation	

opening permitted is a manway located at the top. The valve arrangement is the same as that on railway tank cars. Immediately below each liquid angle valve are an excess-flow valve and an eduction pipe the same as those on tank cars. The safety relief valve is of

TABLE 5 TANK MOTOR VEHICLE SPECIFICATIONS

TC* Specification Number	Description
TC331 (or MC331)	Seamless or welded steel tank. Design and construct in accordance with ASME Code. One opening with protective housing and manway cover. Maximum design pressure 3450 kPa (500 psi). Insulated. Postweld heat treatment as per ASME Code. Gauging device prohibited.

* Transport Canada

the spring-loaded type combined with a breaking pin assembly. On all tanks, the pin is designed to function at 110 percent of the tank design pressure. One or more frangible discs set to operate at a pressure less than twice and more than 1.5 times design pressure is required. Also, one or more pressure controlling devices is required in addition to the safety relief valve (TDGC 1980). A pressure gauge, complete with shut-off valve, is also required (TDGC 1980).

4.2 Off-loading

4.2.1 Off-loading Equipment and Procedures for Cylinders. The following points should be observed when handling and storing cylinders:

- Valve protection hoods should be in place.
- Containers should not be stored near ventilating systems.
- Store to minimize external corrosion.
- Store cylinders upright and fixed by chairs.
- Store full and empty containers separately.
- Flexible copper connection between the cylinder and the piping system should be used (HCG 1981).

4.2.2 Off-loading Equipment and Procedures for Railway Tank Cars and Tank Motor Vehicles. Railway tank cars and tank motor vehicles are basically off-loaded in the same manner but only after the following precautionary steps have been undertaken:

- Unloading operations to be performed only by properly instructed personnel.
- Dead-end siding used only for carbon dioxide rail cars should be provided.

- Brakes must be set, wheels chocked, proper derails employed and caution placards placed.
- Suitable operating platform to be provided at unloading point.

The railway tank car or highway vehicle may be unloaded by pump or compressor (HCG 1981). When using the pumping method, liquid is pumped from one of the two liquid angle valves. When gas is required, carbon dioxide gas is discharged from the gas angle valves.

During the compressor method, a suction line from the storage tank vapour space discharges to a compressor which forces compressed carbon dioxide gas into the tank car. The pressure on the car should never exceed the service pressure at which the safety valve is set to operate.

4.2.3 Specifications and Materials for Off-loading Equipment. Under this section, the components of a typical off-loading system handling dry liquid carbon dioxide at commonly employed temperatures and pressures will be discussed. These include pipes and fittings, flexible connections, valves, gaskets, pumps and storage tanks.

Pipes and fittings should be of Schedule 80 threaded steel pipe. Alternately, stainless steel, copper, brass or seamless carbon steel may be used. If carbon dioxide is wet, stainless steel, Hastelloy or Monel is required (GPD).

Pipeline joints should preferably be flanged or welded. If threaded joints are necessary, extreme care must be taken to obtain clean, sharp pipe threads, in order to ensure pressure-tight joints. Flanges should be forged steel rated at 900 kg (2000 lb.) (HCG 1981).

Flexible connectors, consisting of a loop of copper tubing, should be installed between cylinders and rigid piping systems. Seamless copper water tube per ASTM B88 in the annealed state with Type K wall thickness, or heavier, is recommended. Connectors for railway tank cars and motor vehicles may be high pressure hose or an expansion loop composed of threaded elbows.

O.S. and Y or rising stem valves having black iron, drop-forged carbon steel, or bronze bodies, and stems and trim of Monel metal or Hastelloy C nickel alloy are recommended for carbon dioxide service. Glands should be bolted rather than screwed, since the threads of the latter may be quickly attacked by wet carbon dioxide vapour (HCG 1981).

Rubber gaskets are acceptable for liquid or gas service providing a temperature of 60°C is not exceeded (GF). Table 6 lists alternatives.

A jacketed steel magnetic drive centrifugal pump with "wet end" material of carbon steel may be used for pumping dry carbon dioxide. "Wet end" should be stainless steel for wet carbon dioxide.

Steel storage tanks or special refrigerated pressure vessels of up to 414 tonnes capacity are in service (CD 1975). Medium sized tanks have a 29 tonne capacity (CD 1975).

Insulated vessels, along with automatic controls, refrigerator and vaporizer, are sometimes enclosed in a metal housing. Such packages are usually available in 5 tonne capacity, although facilities up to 90 tonnes are available in this form (CSS).

4.3 Compatibility with Materials of Construction

The compatibility of carbon dioxide with materials of construction is indicated in Table 6. The unbracketed abbreviations are described in Table 7. The rating system for this report is briefly described below.

Recommended: This material will perform satisfactorily in the given application.

Conditional: Material will show deterioration in the given application; however, it may be suitable for intermittent or short-term service.

Not Recommended: Material will be severely affected in this application and should not be used.

TABLE 6 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
1. Pipes and Fittings	Wet Gas or Aqueous Solution	60	PVC I PVC II (DPPED 1967)		
	Gas	79	PVDC (DCRG 1978)		
	Gas	107	PP (DCRG 1978)		
	Gas	121	Chlorinated Polyether (DCRG 1978)		
	Gas	135	PVDF (DCRG 1978)		

TABLE 6 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
1. Pipes and Fittings (cont'd)	Gas	To operating limit of material	ABS PE (MWPP 1978)	PVC I	
2. Valves	All	All	SS 316 (JSSV 1979)		
3. Others	Dry, 100%	60	uPVC, PE, PP, POM, NR, NBR, IIR, EPDM, CR, FPM, CSM (GF)		
	All, Moist	60	PE, PP, POM, NR, NBR, IIR, EPDM, CR, FPM, CSM (GF)	uPVC (GF)	
	Wet or Dry	60	PVC (TPS 1978)		
	Wet or Dry	66	PP (TPS 1978)		
	Dry, 100%	80	PP, NBR, IIR, EPDM, CR, FPM, CSM (GF)	PE POM (GF)	uPVC NR (GF)
	Wet or Dry	85	CPVC (TPS 1978)		
	All, Moist	100	NBR, IIR, EPDM, CR, FPM, CSM (GF)	PE PP (GF)	uPVC, POM NR (GF)
3. Others (cont'd)	Wet or Dry	121	PVDF (TPS 1978) SBR, Si (GPP)		
	100%	24-371	Glass (CDS 1967)		
	100%	52	Concrete Wood (CDS 1967)		

TABLE 7 MATERIALS OF CONSTRUCTION

Abbreviation	Material of Construction
ABS	Acrylonitrile Butadiene Styrene
	Carbon Steel
	Chlorinated Polyether
CPVC	Chlorinated Polyvinyl Chloride
CR	Polychloroprene (Neoprene)
CSM	Chlorosulphonated Polyethylene (Hypalon)
	Copper
EPDM	Ethylene Propylene Rubber
FPM	Fluorine Rubber (Viton)
	Glass
IIR	Isobutylene/Isoprene (Butyl) Rubber
NBR	Acrylonitrile/Butadiene (Nitrile, Buna N) Rubber
NR	Natural Rubber
	Nickel-Copper Alloy (Monel)
	Nickel-Molybdenum (Hastelloy Alloy C)
PE	Polyethylene
POM	Polyoxymethylene
PP	Polypropylene
PVC (followed by grade)	Polyvinyl Chloride
PVDC	Polyvinylidene Chloride
PVDF	Polyvinylidene Fluoride
	Silicon
SS (followed by grade)	Stainless Steel
SBR	Styrene-Butadiene (GR-S, Buna S) Rubber
uPVC	Unplasticized Polyvinyl Chloride
	Wood

5 CONTAMINANT TRANSPORT

5.1 General Summary

Spills of liquefied carbon dioxide on the soil would probably be in the solid form. Once on the soil, little penetration or absorption of the material is expected. The evaporation of the solid (and liquid) is such that little carbon dioxide would ever reach groundwater. For this reason, no nomograms for soil penetration have been prepared.

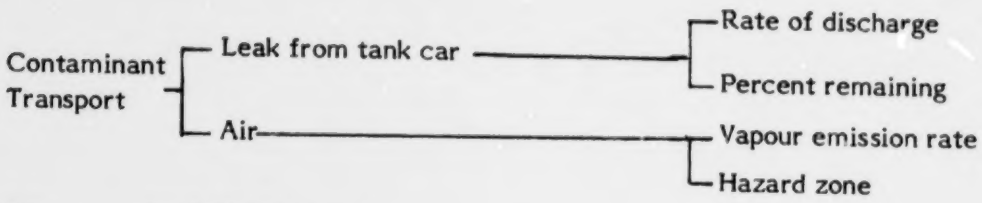
The solidification behaviour of liquefied carbon dioxide can also take place at punctures in containment vessels. This could dramatically slow the leak rate. Furthermore, if a vessel is punctured above the liquid level, the evaporative cooling of the rapid vapour release may cool the liquid contents sufficiently to produce the solid. In this event, the evaporation rate (actually the sublimation rate) will be much slower than when liquid is present. It is felt that these effects could combine with environmental factors to produce leak rates below what is given in the following section. The leak rates may be up to one order of magnitude slower (10 times) than predicted if the ambient temperature is low and the insulation of the vessel is fairly intact. The leak rates may be up to two or three orders of magnitude slower than predicted if some solid forms in the puncture. In any event, the leak rate nomograms provide the most rapid (worst-case) situation.

Liquefied carbon dioxide behaves somewhat uniquely when released from a container; in most cases, the solid is formed in the form of "snow". The solid in most cases is aerated (as a result of its release in air) and thus has a density less than the regular solid (dry ice). Vapour release from both the snow and dry ice is primarily by sublimation - direct transition from the solid to vapour phase. The liquid form is rarely seen in a spill situation.

When spilled on water, liquefied carbon dioxide will probably be in a solid form or will rapidly evaporate, forming small residual amounts of solid due to evaporative cooling. The residual amounts of solid will partly evaporate and partly dissolve in the water. This behaviour is difficult to model and thus no nomograms are presented here.

Vapour plumes from carbon dioxide spills will only be visible if the vapour released is sufficiently cold to condense humidity in the air, producing visible (white) water droplets. This will occur in the case of massive spills of liquefied or solid carbon dioxide and in situations where the relative humidity is high. Carbon dioxide vapour is heavier than air and thus the vapour cloud will move along the ground, in cases of poor mixing, it will displace the air.

The following factors are considered for the transport of a carbon dioxide spill in the air, water and soil media:



5.2 Leak Nomograms

5.2.1 Introduction. Carbon dioxide is commonly transported as a liquefied compressed gas. While the capacities of the railway tank cars vary widely, one size has been chosen throughout the EnviroTIPS series for development of the leak nomograms. It is approximately 2.75 m in diameter and 13.4 m long, with a carrying capacity of about 80 000 L.

If a tank car loaded with liquefied carbon dioxide is punctured on the bottom, all of the contents are presumed to drain out to provide a worst case estimate. As noted above, the solid will probably be formed and could in some case slow the leak rate or even plug the leak entirely.

If the tank car is punctured in the top or at any point above the liquid level, it is assumed that gas will be vented until all of the liquid has vaporized and the internal and external tank pressures have equalized. For the purposes of nomogram preparation, the liquid is assumed to remain at a constant temperature (isothermal) equal to the ambient temperature (T). Consequently, the venting rate (q) is assumed to be constant until all of the liquid is vaporized. The assumed maximum tank ambient temperature is -23°C, yielding a saturated vapour pressure (P_{sat}) of 2200 kPa. This pressure approximates the setting of the pressure regulating valves on tank cars normally used to transport carbon dioxide.

The assumption of isothermal conditions, which maximize the gas release rate from the tank, will generally provide worst case values. As was noted above, in many spill situations the natural leak rate could be many times slower.

5.2.2 Nomograms.

5.2.2.1 Bottom puncture - liquid venting.

Figure 11: Percent remaining versus time. Figure 11 provides a means of estimating the percent of carbon dioxide remaining in the standard tank car after the time of puncture, for a number of different hole diameters. The hole diameter is actually an equivalent diameter and can be applied to a noncircular puncture.

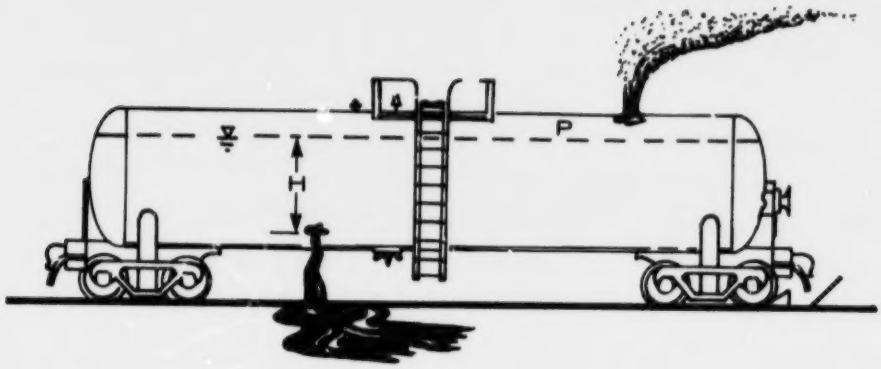


FIGURE 10 TANK CAR WITH PUNCTURE HOLE IN BOTTOM OR TOP

The standard tank car (2.75 m Ø x 13.4 m long) is assumed to be initially full (at t=0) with a volume of about 80 000 L of carbon dioxide at -23°C. The amount remaining at any time (t) is not only a function of the discharge rate over time, but also of the size and shape of the tank car.

Figure 12: Discharge rate versus puncture size. Figure 12 provides a means of estimating the maximum discharge rate (L/s) for a number of equivalent hole diameters. As the pressure force dominates the gravitational force, the discharge rate remains relatively constant as the tank empties.

5.2.2.2 Top puncture - gas venting.

Figure 13: Percent remaining versus time. Figure 13 provides a means of estimating the percent of carbon dioxide remaining in the standard tank car after the time of puncture, for a number of different hole diameters. The hole diameter is actually an equivalent diameter and can be applied to a noncircular puncture. As isothermal conditions have been assumed, the internal pressure and venting rate are constant.

Figure 14: Discharge rate versus puncture size. Figure 14 presents the relationship between discharge rate (kg/s) and the equivalent diameter of the hole for gas venting above the liquid level in the tank car. For any one hole size, the venting rate is assumed to be constant until all the liquid is vaporized. This is consistent with the assumption of isothermal conditions in the tank and results in a conservative estimate of the gas venting rate.

The values presented in Figure 14 are independent of the tank car size, but assume that the temperature of the liquid is -23°C, yielding a saturated vapour pressure of 2200 kPa.

FIGURE 11

CARBON DIOXIDE

PERCENT REMAINING vs TIME

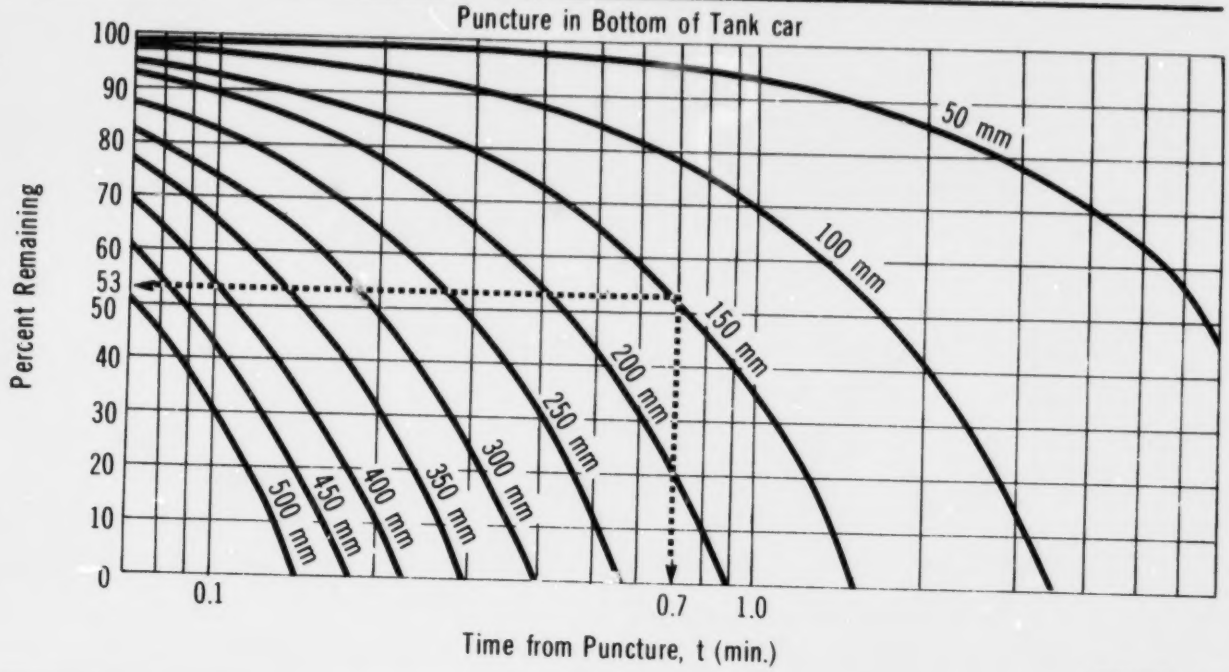


FIGURE 12

CARBON DIOXIDE

DISCHARGE RATE vs PUNCTURE SIZE

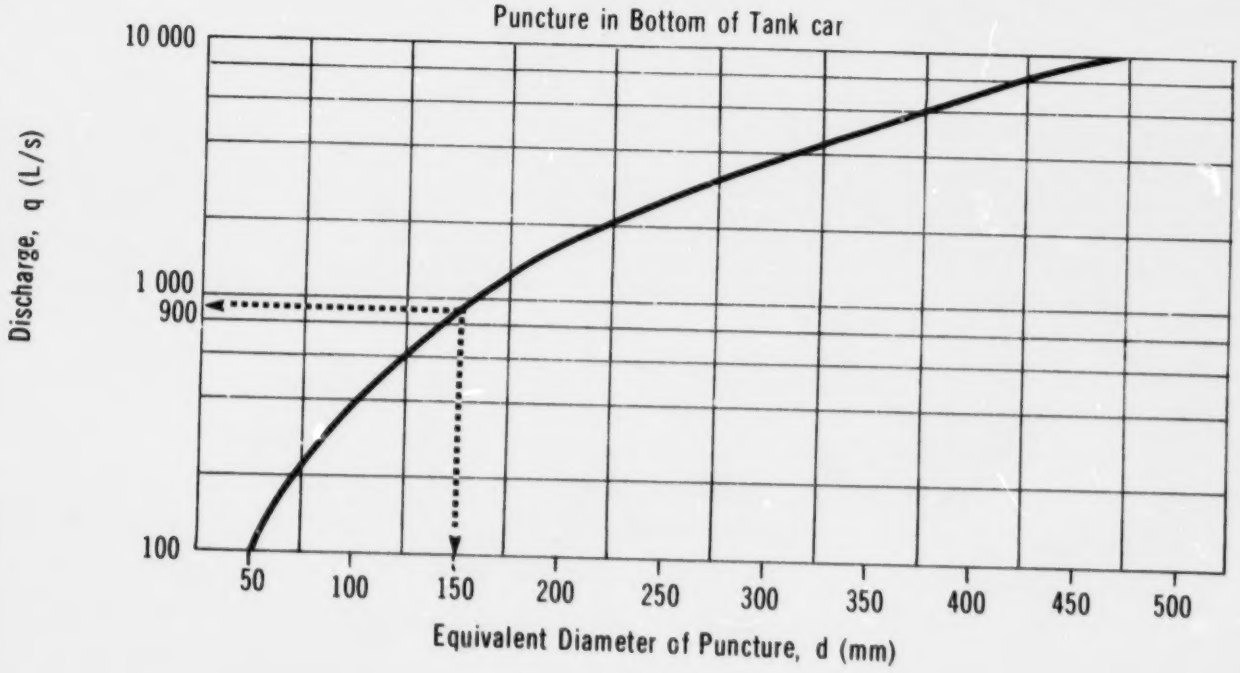


FIGURE 13

CARBON DIOXIDE

PERCENT REMAINING vs TIME

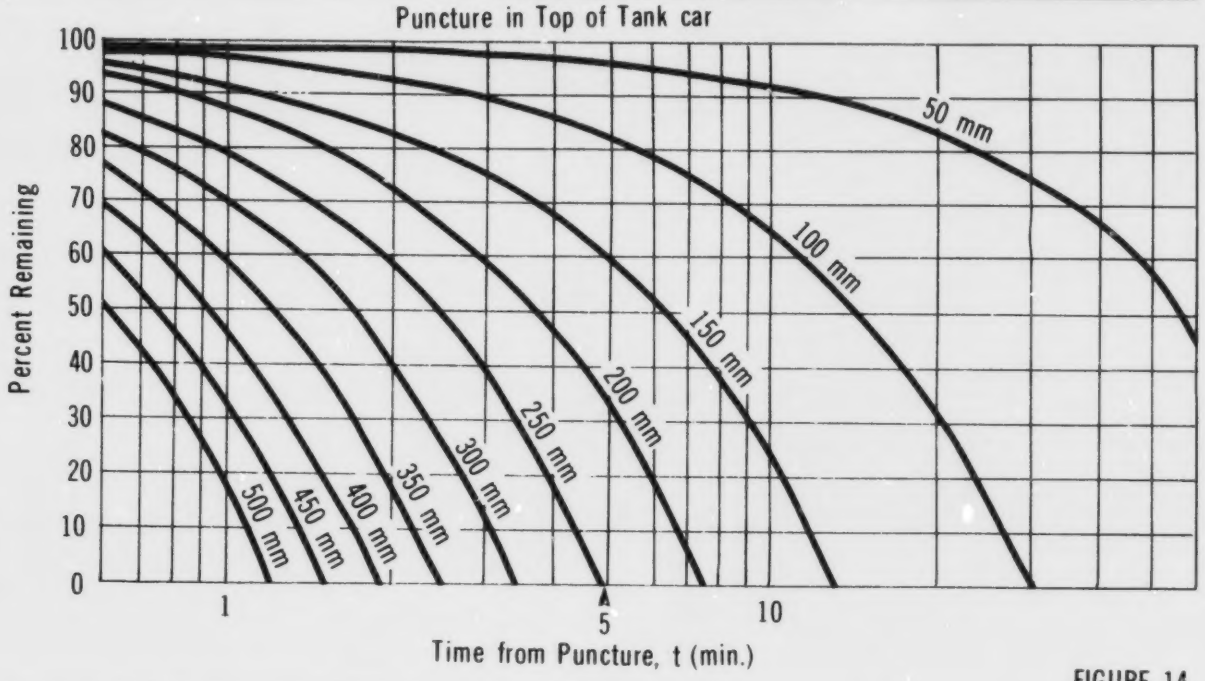
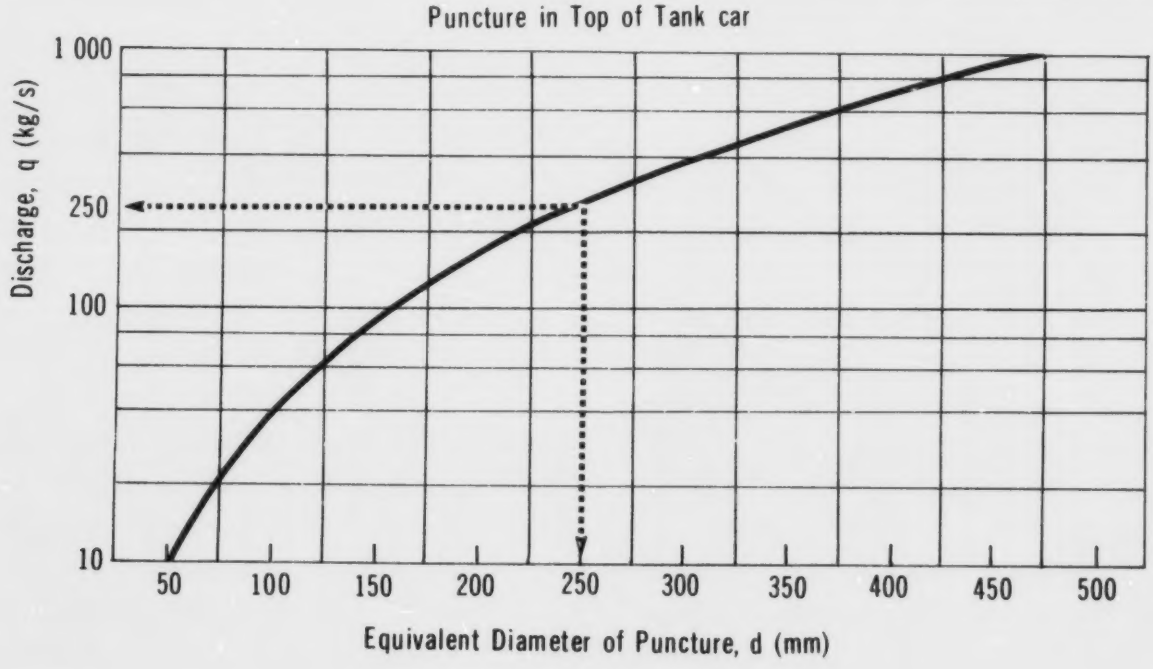


FIGURE 14

CARBON DIOXIDE

DISCHARGE RATE vs PUNCTURE SIZE



5.2.3 Sample Calculations.

i) Problem A

The standard tank car filled with carbon dioxide at -23°C has been punctured on the bottom. The equivalent diameter of the hole is 150 mm. What percent of the initial 80 000 L remains after 0.7 min and what is the instantaneous discharge rate from the tank?

Solution to Problem A

Step 1: Calculate amount remaining at t=0.7 min

- Use Figure 11
- With t=0.7 min and d=150 mm, the amount remaining is about 53 percent or 42 000 L

Step 2: Calculate the discharge rate

- Use Figure 12
- With d=150 mm, the instantaneous discharge rate (q)=900 L/s

ii) Problem B

The standard tank car in Problem A has been punctured above the liquid level. The equivalent diameter of the orifice is estimated at 250 mm. How long will it take to empty the tank car and what is the release rate, assuming isothermal conditions?

Solution to Problem B

Step 1: Calculate the time to empty

- Use Figure 13
- With d=250 mm, the tank empties (0 percent remaining) in approximately 5 min

Step 2: Calculate the discharge rate

- Use Figure 14
- With d=250 mm and assuming isothermal conditions, the venting rate is constant at 250 kg/s

5.3 Dispersion in the Air

5.3.1 Introduction. Since liquefied carbon dioxide under pressure is an extremely volatile liquid, vapour released from a liquid pool spilled on a ground or water surface evaporates rapidly enough to consider the spill as producing instantaneous vapour in the form of a puff. Similarly, the solid also produced in a typical spill situation would sublime rapidly at first. Only this type of vapour release is treated here.

To estimate the vapour concentrations downwind of the accident site for the determination of the toxicity hazard zone, the atmospheric transport and dispersion of the contaminant vapour must be modelled. The models used here are based on Gaussian formulations and are the ones most widely used in practice for contaminant concentration predictions. The model details are contained in the Introduction Manual.

Figure 15 depicts schematically the contaminant plume configuration from a "puff" surface release. The dispersion model represents the spill as an instantaneous point source (with a total vapour release quantity, Q_T) equal to the amount of contaminant spilled.

It should be noted that a carbon dioxide vapour cloud arising from cold bulk liquid behaves as a heavier-than-air gas since the density of the vapour cloud is greater than that of air (1.5 times that of air at 20°C) and due to the fact that the vapour cloud arising from the cold bulk liquid will be cold itself. Ground hugging and gas accumulation in low-lying areas may therefore be observed during the initial period. Conventional Gaussian modelling will tend to depict heavier-than-air plumes (puffs) to be narrower than observed.

5.3.2 Vapour Dispersion Nomograms and Tables. The aim of the air dispersion nomograms is to define the hazard zone due to toxicity of a vapour cloud. The following nomograms and data tables are contained in this section (to be used in order given):

Table 8: weather conditions

Figure 17: normalized vapour concentration as a function of downwind distance and weather conditions

Table 9: maximum puff hazard half-widths

Figure 19: vapour puff travel distance as a function of time elapsed since the spill and wind speed

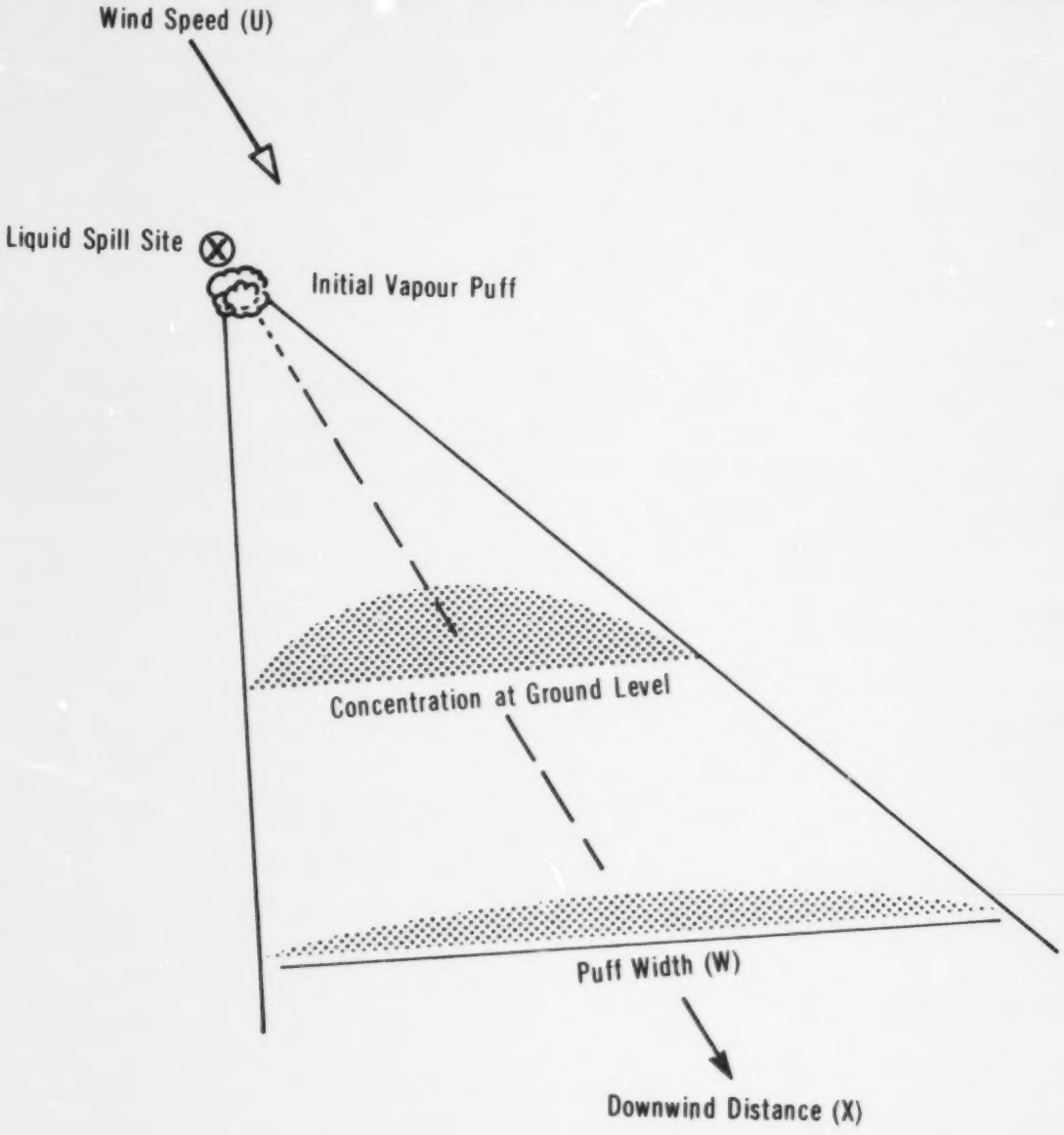
The flow chart given in Figure 16 outlines the steps necessary to make vapour dispersion calculations and identifies the nomograms or tables to be used. This section deals only with the portion contained within the dashed box. Data on "total liquid discharged" is contained in Section 5.2. A description of each vapour dispersion nomogram and its use follows.

5.3.2.1 Figure 17: Vapour concentration versus downwind distance. Figure 17 shows the relationship between the vapour concentration and the downwind distance for weather conditions D and F. The nomograms were developed using the dispersion models described in the Introduction Manual. The vapour concentration is represented by the

FIGURE 15

CARBON DIOXIDE

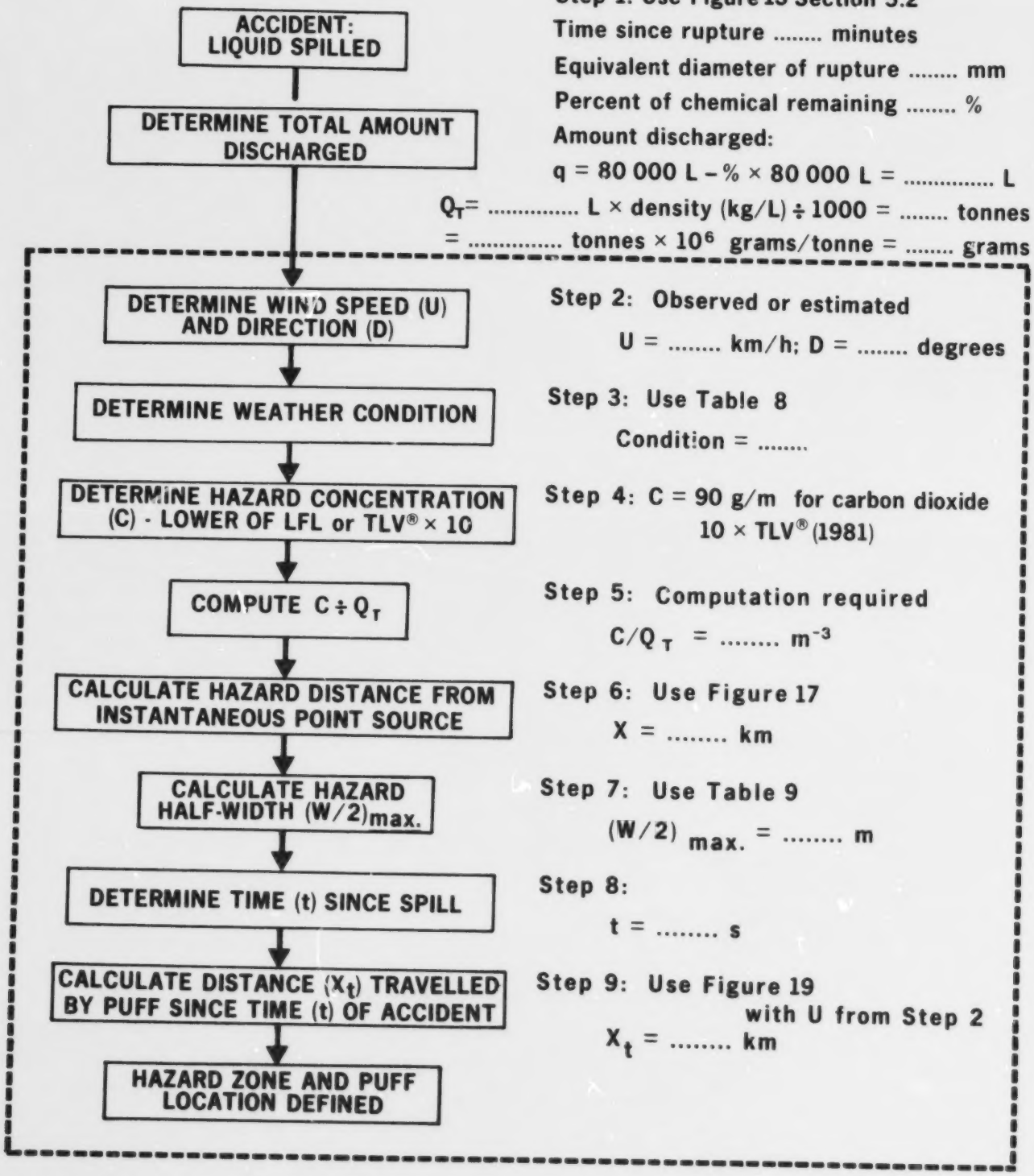
SCHEMATIC OF CONTAMINANT PUFF



CARBON DIOXIDE

FIGURE 16

FLOW CHART TO DETERMINE VAPOUR HAZARD ZONE


ACCIDENT: LIQUID SPILLED
DETERMINE TOTAL AMOUNT DISCHARGED
DETERMINE WIND SPEED (U) AND DIRECTION (D)
DETERMINE WEATHER CONDITION
DETERMINE HAZARD CONCENTRATION (C) - LOWER OF LFL or TLV® × 10
COMPUTE C ÷ Q_T
CALCULATE HAZARD DISTANCE FROM INSTANTANEOUS POINT SOURCE
CALCULATE HAZARD HALF-WIDTH $(W/2)_{max.}$
DETERMINE TIME (t) SINCE SPILL
CALCULATE DISTANCE (X_t) TRAVELLED BY PUFF SINCE TIME (t) OF ACCIDENT
HAZARD ZONE AND PUFF LOCATION DEFINED

Step 1: Use Figure 13 Section 5.2

Time since rupture ..... minutes

Equivalent diameter of rupture ..... mm

Percent of chemical remaining ..... %

Amount discharged:

q = 80 000 L – % × 80 000 L = ... L

Q_T = ... L × density (kg/L) ÷ 1000 = ... tonnes

= ..... tonnes × 10^6 grams/tonne = ... grams

Step 2: Observed or estimated

U = ... km/h; D = ... degrees

Step 3: Use Table 8

Condition = ...

Step 4: C = 90 g/m for carbon dioxide

10 × TLV® (1981)

Step 5: Computation required

C/Q_T = ... m^{-3}

Step 6: Use Figure 17

X = ... km

Step 7: Use Table 9

$(W/2)_{max.}$ = ... m

Step 8:

t = ... s

Step 9: Use Figure 19

with U from Step 2

X_t = ... km

TABLE 8 WEATHER CONDITIONS

Weather Condition F	Weather Condition D
Wind speed <11 km/h (≈3 m/s) and one of the following: - overcast day - night time - severe temperature inversion	Most other weather conditions

normalized, ground-level concentration (C/Q_T) at the centreline of the contaminant puff. Weather condition F is the poorest for dispersing a vapour cloud and condition D is the most common in most parts of Canada. Before using Figure 17, the weather condition must be determined from Table 8.

Use: The maximum hazard distance, X, downwind of the spill can be calculated from Figure 17 knowing:

- Q_T, the mass of vapour emitted (equivalent to liquid spilled)
- U, the wind speed (m/s)
- the weather condition
- the hazard concentration limit, C, which is the value of 10 times the Threshold Limit Value• (TLV in g/m^3). Note: To convert the TLV•, in ppm, to a concentration in g/m^3, use Figure 18.

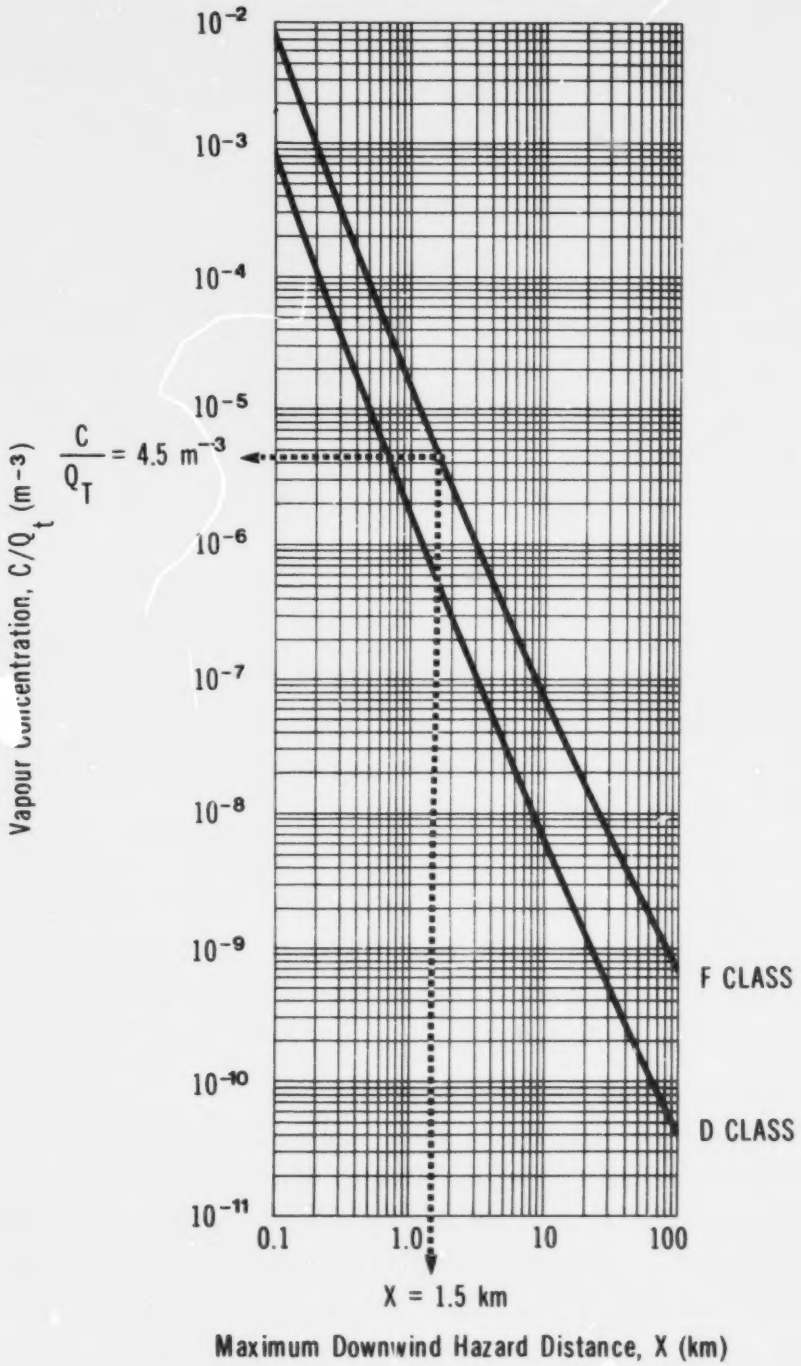
A hazard concentration limit of 10 times the TLV• has been arbitrarily chosen as it represents a more realistic level at which there would be concern for human health on the short term (i.e., on the order of 30 minutes). The TLV• is a workplace standard for long-term exposure. Use of this value as the hazard limit would result in unrealistically large hazard zones.

5.3.2.2 **Table 9: Maximum puff hazard half-widths.** This table presents data on the maximum puff hazard half-widths, $(W/2)_{max}$, for a range of Q_T values under weather conditons D and F. These data were computed using the dispersion modelling techniques given in the Introduction Manual for a value of 10 times the carbon dioxide Threshold Limit Value (TLV•) of 9.0 g/m^3, or 90 g/m^3. The maximum puff hazard half-width represents the maximum half-width of the carbon dioxide vapour cloud, downwind of the spill site, corresponding to a hazard concentration limit of 10 x TLV•. Table 9 is

FIGURE 17

CARBON DIOXIDE

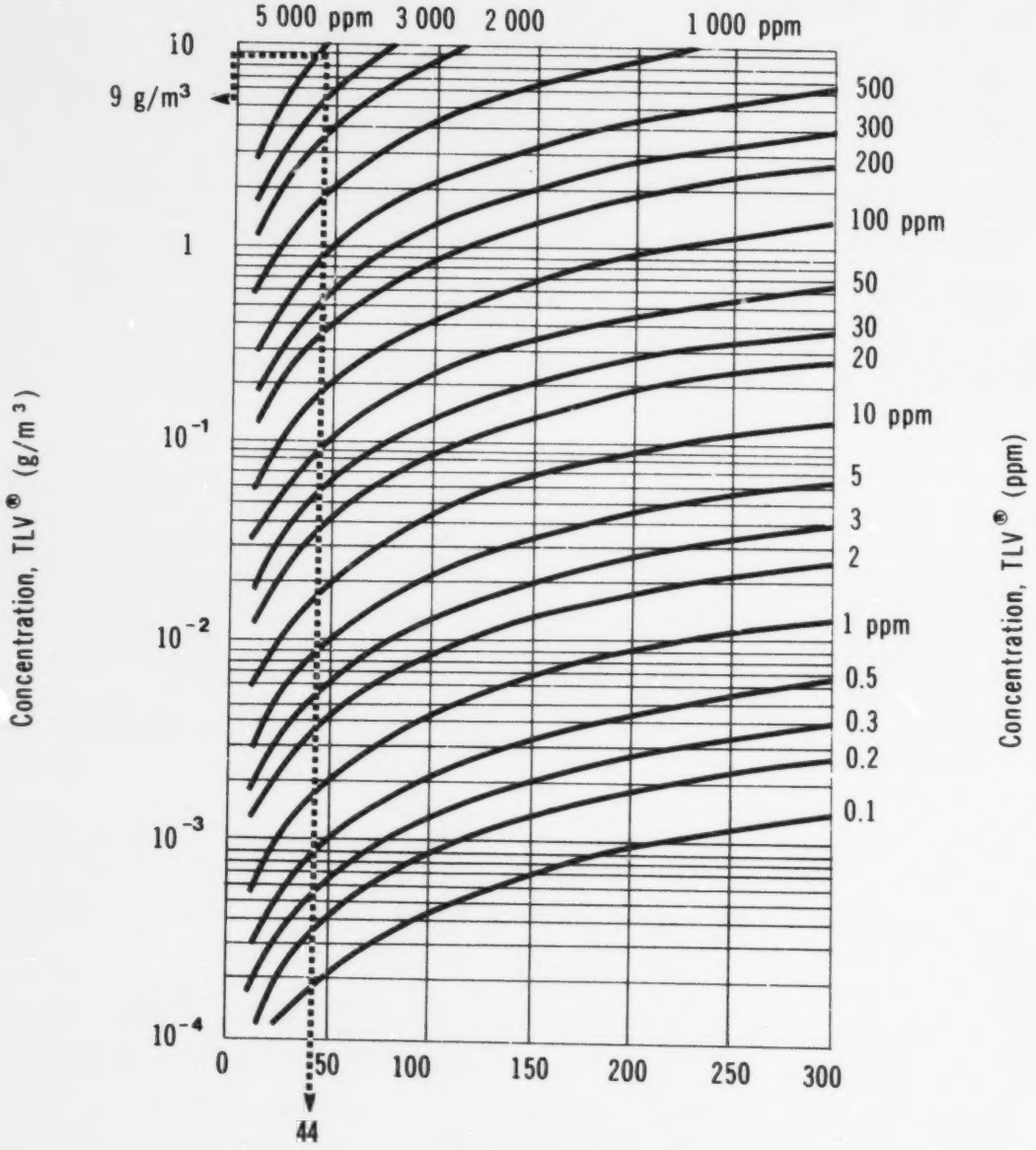
NORMALIZED VAPOUR CONCENTRATION VS DOWNWIND DISTANCE



CARBON DIOXIDE

FIGURE 18

CONVERSION OF THRESHOLD LIMIT VALUE (TLV®) UNITS (ppm to g/m³)



Example: Carbon Dioxide, MW = 44, TLV® = 5 000 ppm, then TLV® in $gm^3 \simeq 9$

Note: data applicable at 25° and 760 mm Hg pressure

TABLE 9 MAXIMUM PUFF HAZARD HALF-WIDTHS (For carbon dioxide)

Weather Condition D			Weather Condition F		
Q_T (tonnes)	$(W/2)_{max}$ (m)		Q_T (tonnes)	$(W/2)_{max}$ (m)	
2 750 000	3 950	(97.2 km)*	135 000	1 860	(99.5 km)*
2 500 000	3 810		125 000	1 800	
2 000 000	3 500		100 000	1 640	
1 500 000	3 130		75 000	1 450	
1 000 000	2 680		50 000	1 220	
750 000	2 400		25 000	905	
500 000	2 060		10 000	610	
400 000	1 890		5 000	455	
300 000	1 690		2 500	350	
200 000	1 450		1 000	245	
150 000	1 300		500	185	
100 000	1 110		250	140	
75 000	1 000		100	100	
50 000	850		50	75	
25 000	660		25	60	
10 000	475	Q = 20 tonnes →	20	55	→ $(W/2)_{max}$ = 55 m
5 000	365		10	45	
1 000	200		5	35	
500	155		1	20	
250	120				
100	85				
50	70				
25	55				
20	50		* Data are provided up to a maximum downwind hazard distance of 30 km		
10	40				
5	30				
1	20				

Example: Under weather condition F and Q_T = 20 tonnes, then puff hazard half-width $(W/2)_{max}$ = 53 m

Note: Above table is valid only for a carbon dioxide concentration of 10 x TLV•, or 90 g/m^3

therefore only applicable for a carbon dioxide hazard concentration limit of 10 x TLV• or 90 g/m^3. Also, data are provided up to a maximum hazard distance downwind of 100 km.

Under weather condition D, the wind speed (U) range applicable is 1 to 30 m/s. The range of instantaneous vapour emission rates (Q_T) used was 1 to 2 750 000 tonnes, respectively. If the entire contents of an 80 000 L (17 600 Imp. gal.) tank car spill, the mass spilled would be 88 000 kg or approximately 88 tonnes. Under class D of Table 9, data are provided for up to 31 000 times this amount to allow for the modelling of most spill situations.

Under weather condition F, the wind speed (U) range applicable is 1 to 3 m/s. The range of instantaneous vapour emission rates (Q_T) used was 1 to 135 000 tonnes, respectively. Therefore, under class F of Table 9, data are provided for up to 1500 times a standard rail car load.

Use: Knowing the weather condition and Q_T, pick the closest value in the table and the corresponding $(W/2)_{max}$, the maximum puff hazard half-width, in metres. (For an intermediate value, interpolate Q_T and $(W/2)_{max}$ values.) Also refer to the example at the bottom of Table 9.

5.3.2.3 Figure 19: Puff travel time versus travel distance. Figure 19 presents plots of puff travel time (t) versus puff travel distance (X_t) as a function of different wind speeds (U). This is simply the graphical presentation of the relationship $X_t = Ut$ for a range of typical wind speeds.

Use: Knowing the time (t) since the spill occurred and the wind speed (U), the distance (X_t) can be determined which indicates how far downwind the puff has travelled.

5.3.3 Sample Calculation. The sample calculation given below is intended to outline the steps required to estimate the downwind hazard zone which could result from a spill of liquid carbon dioxide. The user is cautioned to take note of the limitations in the calculation procedures described herein and in the Introduction Manual. The estimates provided here apply only for conditions given. It is recommended that the user employ known or observational estimates (i.e., of the spill quantity) in a particular spill situation if possible.

Problem:

During the night, at about 2:00 a.m., 20 tonnes of liquid carbon dioxide were spilled on a flat ground surface. It is now 2:05 a.m. The temperature is 20°C and the wind is from the NW at 7.5 km/h. Determine the extent of the vapour hazard zone.

Solution:

Step 1: Quantity spilled is given, $Q_T = 20$ tonnes

- $Q_T = 20$ tonnes or 20×10^6 g
- $Q_T = 2 \times 10^7$ g

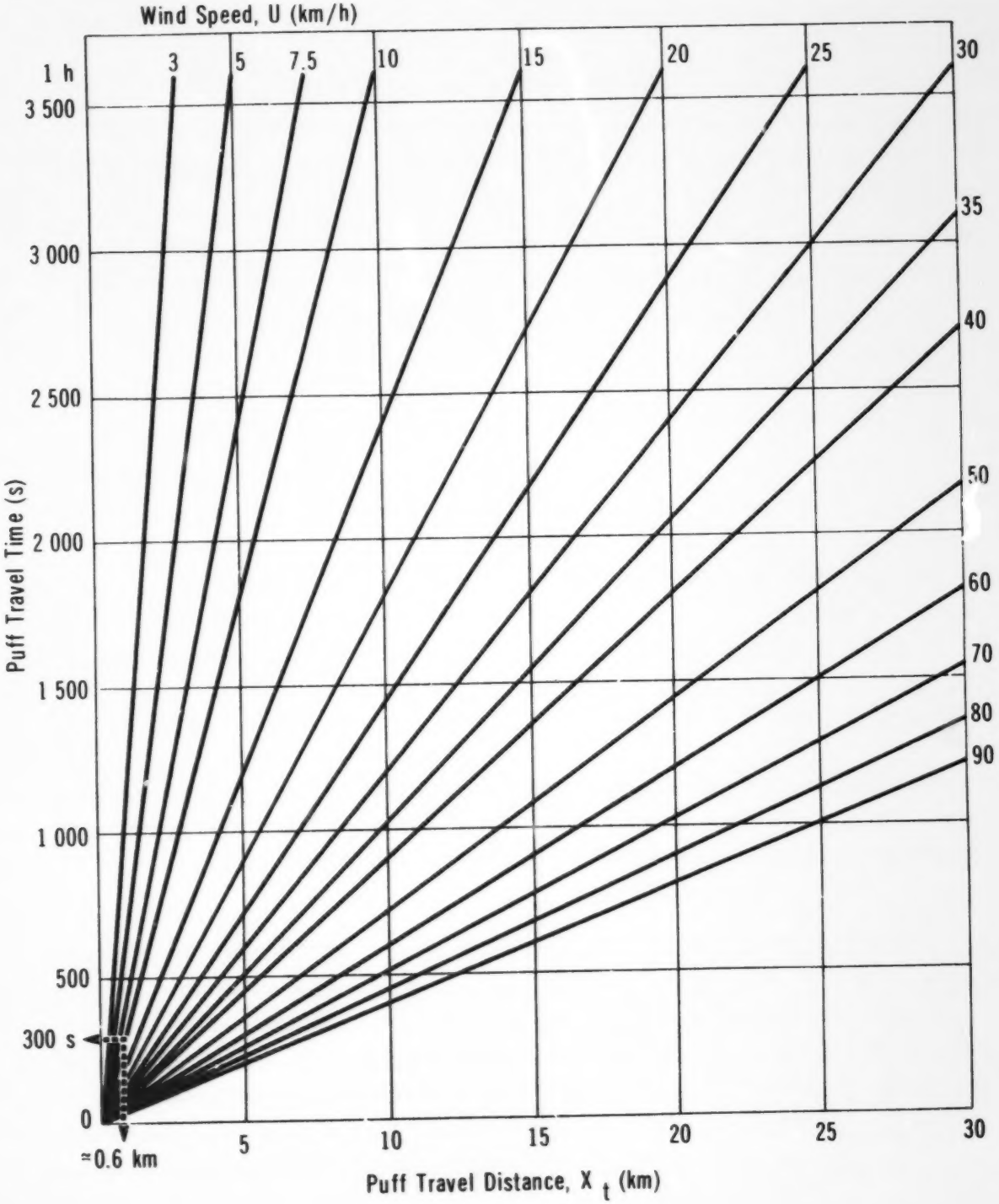
Step 2: Determine the wind speed (U) and direction (D)

- Use available weather information, preferably on-site observations
- Given: U = 7.5 km/h, then U = 7.5 ÷ 3.6 = 2.1 m/s
  D = NW or 315° (D = Direction from which wind is blowing)

FIGURE 19

CARBON DIOXIDE

PUFF TRAVEL TIME VS TRAVEL DISTANCE



Step 3: Determine the weather condition

- From Table 9, weather condition F = since U is less than 11 km/h and it is night

Step 4: Determine the hazard concentration limit (C)

- This is 10 times the TLV•, C = 90 g/m^3 (TLV• = 9.0 g/m^3)

Step 5: Compute C/Q_T

- $C/Q_T = \frac{90}{2 \times 10^7} = 4.5 \times 10^6$ m^{-3}

Step 6: Calculate the hazard distance (X) from the instantaneous point source

- From Figure 17 with $C/Q_T = 4.5 \times 10^{-6}$ m^{-3} and weather condition F, X ≈ 1.5 km

Step 7: Calculate the puff hazard half-width $(W/2)_{max}$

- Use Table 9
- With Q_T = 20 tonnes
- Then for weather condition F, $(W/2)_{max}$ = 55 m

Step 8: Determine the time since the spill

- t = 5 min x 60 = 300 s

Step 9: Calculate the distance travelled (X_t) by the vapcur puff since the time of the accident

- Using Figure 19, with t = 300 s and U = 7.5 km/h, then X_t = 0.6 km (more accurately from X_t = Ut = 2.1 m/s x 300 s = 630 m = 0.63 km)

Step 10: Map the hazard zone

- This is done by drawing a rectangular area with dimensions of twice the maximum puff hazard half-width (55 m) by the maximum hazard distance downwind of the instantaneous point source (1.5 km) along the direction of the wind, as shown in Figure 20
- If the wind is reported to be fluctuating by 20°C about 315° (or from 315° ± 10°), the hazard zone is defined as shown in Figure 21
- Note that the puff has only travelled 0.63 km in the 5 minutes since the spill. At a wind speed of 7.5 km/h, there remain 7 minutes before the puff reaches the maximum downwind hazard distance of 1.5 km

FIGURE 20

CARBON DIOXIDE

HAZARD AREA FOR STEADY WINDS, EXAMPLE PROBLEM

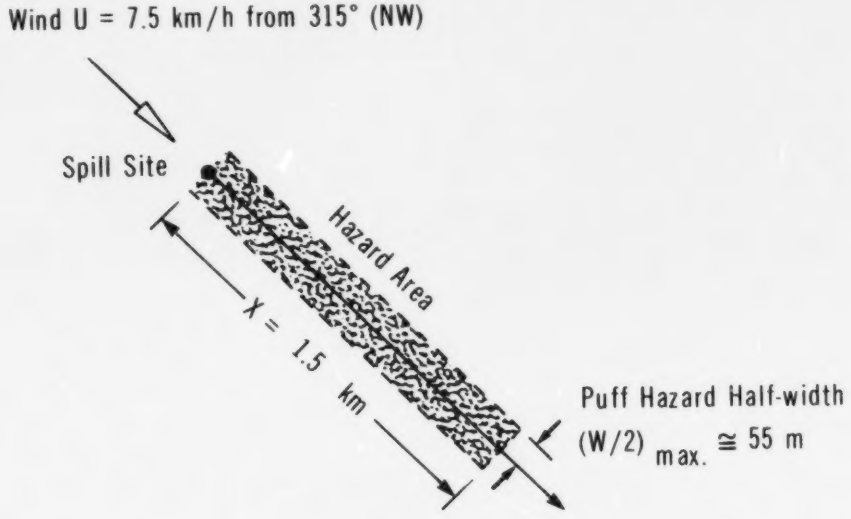
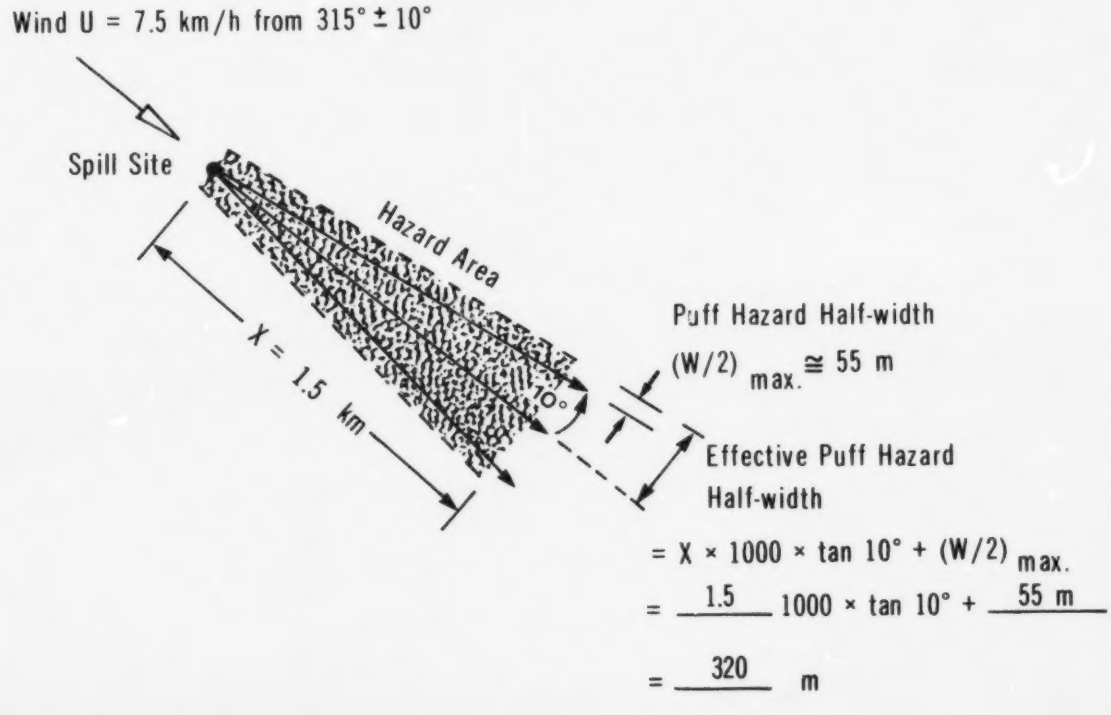


FIGURE 21

CARBON DIOXIDE

HAZARD AREA FOR UNSTEADY WINDS , EXAMPLE PROBLEM


Wind U = 7.5 km/h from 315° ± 10°
Spill Site
Hazard Area
X = 1.5 km
10°
Puff Hazard Half-width
(W/2) max. ≅ 55 m
Effective Puff Hazard Half-width
= X × 1000 × tan 10° + (W/2) max.
= 1.5 1000 × tan 10° + 55 m
= 320 m

6 ENVIRONMENTAL DATA

6.1 Suggested or Regulated Limits

6.1.1 Water. None recommended. Requirements of pH or alkalinity indirectly restrict the carbon dioxide content; the Ontario objective is a pH of 6.5 to 8.5 (Water Management Goals 1978).

6.1.2 Air. No specific limits have been promulgated or recommended in Canada or the United States.

6.2 Aquatic Toxicity

6.2.1 U.S. Toxicity Rating. None assigned.

6.2.2 Measured Toxicities.

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
Fish Kill Data					
45	not stated	Trout	lethal		WQC 1963
200	not stated	Tench	lethal		WQC 1963
100 to 200	rapid	Fish	lethal	adequate oxygen	WQC 1963
50 to 100	not stated	Fish	lethal	less oxygen	WQC 1963
Fish Toxicity Tests					
<20	not stated	Fish	harmful		WQC 1963
1 to 6	not stated	Fish	avoidance behaviour		WQC 1963
12 (yearly average)	not stated	Fish	survival doubtful		WQC 1963
60	not stated	Trout	toxic, but not lethal	low O_2 concentration	WQCDB-2 1971
240	1	Trout	lethal		WQCDB-2 1971
60 to 240	12	Rainbow trout	lethal		WQCDB-2 1971
35	96	Rainbow trout	lethal threshold		WQCDB 1973

Carbonated water has shown no bacterial action against *E. coli* and *E. typhosa* over 40 minutes (WQC 1963).

6.3 Toxicity to Other Biota

6.3.1 Insects. Fruit flies (*Drosophila melanogaster*) remained temporarily paralyzed after exposure to carbon dioxide. Recovery occurred 4 hours after exposure (Clark 1979).

6.3.2 Livestock. Poultry fed with highly carbonated water showed no ill effects (WQC 1963).

6.3.3 Avian. Waterfowl that had inhaled 5 to 8 percent carbon dioxide for 96 hours showed no effects (ERM 1982).

6.3.4 Plants. Carbon dioxide is sometimes used in greenhouses to accelerate plant growth. In one study, doubling of the CO_2 air level resulted in a 30 to 40 percent increase in photosynthetic activity. Another study showed a 50 percent photosynthetic activity increase in corn after a doubling of the CO_2 air level. The effect was found to reach a saturation level (increased CO_2 levels have no increased growth effect) at twice the CO_2 level for corn and at three times the CO_2 level for wheat and soybeans. In numerous growth experiments with pine varieties, CO_2 levels of 3 to 5 times atmospheric levels (normally 300 to 700 ppm) resulted in growth increases of 40 to 80 percent. No studies have been performed to examine the long-term effects of this treatment (Macdonald 1982).

Plants must open the stomata of their leaves in order to allow CO_2 to diffuse from the air to their tissue. During normal summertime conditions, the air in the stomata contains 100 water molecules for every molecule of CO_2. Thus, the plant loses about 100 times the water as it gains CO_2. When the CO_2 concentration in air is increased, it is believed that plants partially close their stomata to compensate. In one experiment, it was shown that when the CO_2 concentration was doubled, photosynthesis increased by 40 percent and water transpiration decreased by 40 percent (Macdonald 1982).

6.4 Effect Studies

In one experiment, rainbow trout were exposed to water containing elevated CO_2 levels (20°C, 15 mm Hg partial pressure CO_2). Fish entering the CO_2 water suffered a sharp decrease in blood pH, significantly reducing O_2 transport by the blood; however, considerable compensation was achieved after a few hours. After a week in high CO_2

water, the trout showed elevated plasma bicarbonate and CO_2 levels and a decrease in plasma chloride. Oxygen transport by the blood was marginally reduced. When returned to normal water, the fish showed a sharp increase in blood pH and a sharp decrease in blood oxygen partial pressure. These values returned to normal after a few hours; plasma bicarbonate and chloride levels took much longer to return to normal (Eddy 1976, 1977).

In another experiment, juvenile sockeye salmon were exposed to lethal levels of gas-saturated water (120, 125 and 130 percent total gas saturation). It was found that mortality was not significantly different at varying CO_2 levels (1.7-220 mg/L CO_2). Mortality (cause of death was determined to be gas bubble disease) was primarily a function of the total gas saturation (Nebeker 1976).

Anchovies were exposed to sudden changes in pH caused by increasing levels of CO_2. Schooling behaviour (swim velocities and direction) was observed to be altered; avoidance behaviour was observed at CO_2 levels just below toxicity levels. Low CO_2 levels did not have much effect (McFarland 1968).

In another experiment, it was found that elevated carbon dioxide levels (16 to 159 µmoles/L) did not increase the growth rate of algae (*Thalassiosira pseudonana*) (Pruder 1979).

6.5 Carbon Dioxide Levels and Dynamics in Water

Carbon dioxide levels in freshwater systems are relatively low, usually less than 5 ppm. The toxicity of CO_2 in freshwater systems is also low, beginning at 10 ppm. Seawater is quite different and may contain CO_2 at levels up to 500 ppm. Since this is close to a saturation level, depending on temperature, little saltwater toxicity work has been done. Its relevance may be low in that marine species are highly tolerant and also because of the buffering action of saltwater. Carbon dioxide levels in marine situations typically vary from 160 to 350 ppm (Kelley 1971). High (or even supersaturated) levels are usually found in areas of upwelling. Low levels are usually found in highly productive bays and inlets. Medium to high levels are typically found where runoff from freshwater streams enters the sea (Longerich 1971). In freshwater systems, the important effect is the decrease in pH with increasing CO_2 concentration. As a rule of thumb, the pH decreases 0.25 units for each doubling of the carbon dioxide partial pressure in the air (Baes 1981).

Carbon dioxide dissolves in water to form hydrated CO_2 and carbonic acid (H_2CO_3). These processes are generally represented by the single reaction:

$$CO_{2(g)} + H_2O \rightleftharpoons H_2CO_3\ (aq.)$$

with the equilibrium condition

$$K_o = \frac{(H_2CO_3)}{P_{CO_2}}$$

where: (H_2CO_3) is the total concentration in the water

P_{CO_2} is the partial pressure in the air

The principal species resulting from carbon dioxide in aquatic systems are anions. The "H_2CO_3" noted above can undergo two reactions:

$$H_2CO_3 \text{ (aq.)} \rightleftharpoons H^+ + HCO_3^-$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}.$$

The "HCO_3^-" is known as the bicarbonate ion and the "CO_3^{2-}" as the carbonate ion. Excess amounts of carbonate ion will lead to the precipitation of calcium carbonate (limestone), thus decreasing (or maintaining constant) the carbonate levels in aquatic systems.

The typical concentrations of these ion species in the ocean are given below (Baes 1981) (concentrations are in mmole/kg):

	(H_2CO_3)	(HCO_3^-)	(CO_3^{2-})
Mixed layer	0.01	2.0	0.2
Deep ocean	0.02	2.3	0.1

6.6 Long-term Fate and Effects

Considerable concern has been expressed in recent years over increasing levels of CO_2 in the air and the possible resulting effects (greenhouse effect). Many data have been published (Lovins 1981; Macdonald 1982; NAS 1979; Williams 1978). The amounts of carbon dioxide expected from spills would not be a problem in this regard. To put this into perspective, it is estimated that 5 gigatons of CO_2 are released per year from fossil fuel burning and 100 gigatons from natural exchange processes (Baes 1981).

7 HUMAN HEALTH

There is a considerable amount of information in the published literature concerning the physiological as well as the toxicological effects of carbon dioxide. Carbon dioxide is an important element in the maintenance of normal body activities, being a factor in the control of respiration, and cerebral circulation, vasodilation and vasoconstriction. When inhaled in elevated concentration, carbon dioxide may act to produce mild narcotic effects, stimulation of the respiratory centre; asphyxiation and even death can occur, depending on the concentration and the duration of exposure. Teratogenic effects in test animals have been reported in the literature. A single study was found implicating carbon dioxide snow (solid carbon dioxide) as a carcinogen when used as a chronic irritant.

Carbon dioxide has been reported in the EPA TSCA inventory. Published work on carbon dioxide toxicology was reviewed in 1976 (NIOSH Crit. 1976). The data summarized here are representative of information in the literature.

The toxicological data summarized here have been extracted from reliable standard reference sources. It should be noted that some of the data are for chronic (long-term), low-level exposures and may not be directly applicable to spill situations.

7.1 Recommended Exposure Limits

The exposure standards for carbon dioxide are based upon its asphyxiant properties. Canadian provincial guidelines generally are similar to those of USA-ACGIH, unless indicated otherwise.

Guideline (Time)	Origin	Recommended Level	Reference
Time-weighted Averages (TWA)			
TLV* (8 h)	USA-ACGIH	5000 ppm (9000 mg/m^3)	TLV 1983
PEL (8 h)	USA-OSHA	5000 ppm (9000 mg/m^3)	NIOSH/OSHA 1981
PEL (10 h)	USA-NIOSH	10 000 ppm	NIOSH Crit. 1976
MAK-D* (8 h 45 min)	Germany (GDR)	9000 mg/m^3	ILO 1980
MAC 8 h	Czech.	9000 mg/m^3	ILO 1980
Short-term Exposure Limits (STEL)			
STEL (15 min)	USA-ACGIH	15 000 ppm (27 000 mg/m^3)	TLV 1983
Ceiling (10 min)	USA-NIOSH	30 000 ppm	NIOSH Crit. 1976

Guideline (Time)	Origin	Recommended Level	Reference
MAK-K** (30 min)	GDR	27 000 mg/m^3	ILO 1980
MAC (10 min)	Czech.	45 000 mg/m^3	ILO 1980
STIL*** (1 h)	-	30 000 ppm	CHRIS 1978
STEL (15 min)	Sask.	18 000 mg/m^3	Sask. 1981
Other Human Toxicities			
IDLH	USA-NIOSH	50 000 ppm	NIOSH Guide 1978
LC_{LO} (1 min)		100 000 ppm	RTECS 1979
TC_{LO}		2000 ppm	ITII 1981

* Maximum average concentration allowed for an 8 h and 45 min workshift
** Maximum concentration allowed for short-term exposure not exceeding 30 min
*** Short-term Inhalation Limit

Inhalation Toxicity Index

The Inhalation Toxicity Index (ITI) is a measure of the potential of a substance to cause injury by inhalation. It is calculated as follows:

ITI = 1315.12 (Vapour Pressure, in mm Hg/TLV*, in ppm)

At 21°C, ITI = 11 398.15

7.2 Irritation Data

7.2.1 Skin Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
Solid carbon dioxide (dry ice)	Causes severe frost burns	NIOSH Crit. 1976

7.2.2 Eye Contact.

Exposure Level (and Duration)	Effects	Reference
Solid carbon dioxide (dry ice)	Causes severe frost burns	NIOSH Crit. 1976
0.03 to 3 percent varying concentrations (Bd)	Causes minor impairment of night vision sensitivity and colour vision for green; all other functions remained the same	Weitzman 1969

7.2.3 Ingestion. No studies have been done on the effects of ingesting carbon dioxide. However, there is no reason to expect that the ingestion of small amounts would cause any harm (FDA 1979).

7.3 Threshold Perception Properties

7.3.1 Odour. Odour Characteristics: Odourless (GE 1979)

7.3.2 Taste. Taste characteristics: At high concentrations, an "acidic taste" is detectable (GE 1979).

7.4 Long-term Studies

7.4.1 Inhalation.

Exposure Level (and Duration)	Effects	Reference
Acute Exposures		
SPECIES: Human		
200 000 to 300 000 ppm (20 to 30 percent)	Unconsciousness and convulsions	Lambertsen 1971. IN NIOSH Crit. 1976
279 000 ppm (25 s)	Unconsciousness	Committee on Aviation Toxicology 1953. IN NIOSH Crit. 1976
170 000 ppm (37 s)	Unconsciousness	Committee on Aviation Toxicology 1953. IN NIOSH Crit. 1976
11 000 to 130 000 ppm (8 to 23 min)	Unconsciousness	Lambertsen 1971. IN NIOSH Crit. 1976
104 000 ppm	Maximum respiration rate	Dripps and Comroe 1947. IN NIOSH Crit. 1976

Exposure Level (and Duration)	Effects	Reference
300 to 104 000 ppm	Graded increases in respiratory minute volume with increased CO_2 concentration	Dripps and Comroe 1947. IN NIOSH Crit. 1976
100 000 ppm (10 percent) (1 min)	LC_{LO}	RTECS 1979
100 000 ppm (5 to 25 min)	Restlessness, confusion, listlessness	Glatte 1967
100 000 to 70 000 ppm	Unconsciousness	Doc. TLV 1981
60 000 ppm (6 to 8 min)	Decreased amplitude of QRS complex of the ECG	Okajima and Simonson 1962. IN NIOSH Crit. 1976
50 000 ppm (30 min)	Intoxication	Doc. TLV 1981
50 000 ppm (5 percent)	Stimulation of respiratory centre	Doc. TLV 1981
30 000 ppm (3 percent)	If O_2 normal, effects slight. If oxygen reduced to <17 percent, ill effects experienced	Doc. TLV 1981
30 000 ppm	Weakly narcotic; blood pressure and pulse increase. Hearing acuity is reduced	Doc. TLV 1981
20 000 ppm (2 percent)	Headache, dyspnea	Doc. TLV 1981
10 000 to 20 000 ppm	Electrolyte balance recovered in 3 to 4 weeks after removal from exposure	Doc. TLV 1981
20 000 ppm	Respiration deepened	Doc. TLV 1981
15 000 ppm (1.5 percent)	Calcium-phosphorus metabolism may be affected	Doc. TLV 1981
6600 ppm	No effect	Doc. TLV 1981
5500 ppm (6 h)	No noticeable symptoms	Doc. TLV 1981
SPECIES: Mammal		
90 000 ppm (5 min)	LC_{LO}	RTECS 1979
SPECIES: Monkey		
100 000 to 600 000 ppm	Twofold increase in respiration rate until 10 percent CO_2. Thereafter, respiration rate decreases until death at concentrations above 60 percent	Stinson and Mattsson 1970. IN NIOSH Crit. 1976

Exposure Level (and Duration)	Effects	Reference
300 000 ppm (10 min)	Stimulation of the brain cortex	Schaefer 1963. IN NIOSH Crit. 1976
300 000 ppm (30 min)	Increased hypothalamus activity	Schaefer 1963. IN NIOSH Crit. 1976
SPECIES: Dog		
300 000 ppm (2 h) followed by 400 000 ppm (2 h)	When exposed to normal air suddenly following CO_2 exposure, cardiac arrhythmias within 0.5-6 min followed by death within 2.5-10 min after the sudden change	Brown and Miller 1952. IN NIOSH Crit. 1976
300 000 ppm	Increased secretion of adrenalin and noradrenalin	Harrison and Seaton 1965. IN NIOSH Crit. 1976
150 000 ppm, 100 000 ppm, 50 000 ppm	Cerebral spinal fluid pressure increases with increased CO_2 concentration	Small et al. 1960. IN NIOSH Crit. 1976
SPECIES: Guinea Pig		
150 000 ppm (6 to 24 h)	Hyaline membrane formation	Schaefer et al. 1964. IN NIOSH Crit. 1976
SPECIES: Rat		
657 190 ppm (15 min)	LC_{LO}	GE 1979
500 000 ppm (1 h)	Extreme edema, recovery 7 d after removal from exposure	Niemoeller and Schaefer 1962. IN NIOSH Crit. 1976
300 000 ppm (5 h)	Extreme edema, recovery 7 d after removal from exposure	Niemoeller and Schaefer 1962. IN NIOSH Crit. 1976
200 000 ppm (30 h)	100 percent mortality	Carter 1959. IN NIOSH Crit. 1976
150 000 ppm (6 h)	Uncompensated respiratory acidosis, pulmonary effusion and changes in the lamellar bodies of granular pneumocytes	Schaefer et al. 1964. IN NIOSH Crit. 1976
100 000 ppm (2 h, 4 h and 8 h)	Degenerative changes in the testes paralleling concentration and duration of exposure	Van Demark et al. 1972. IN NIOSH Crit. 1976

Exposure Level (and Duration)	Effects	Reference
Chronic Exposures		
SPECIES: Human		
60 000 ppm (5 d)	Indication of emotional changes no indication of vigilance, coordination or problem-solving ability decreases	Weybrew 1970
40 000 ppm (10 d)	34 percent increase in blood serotonin levels, returned to normal after a few days	Gordon 1968
30 000 ppm (5 d)	No visible effects, arterial pH decreased to 7.37 from 7.40 temporarily	Glatte 1967
10 000 to 20 000 ppm	Acidosis, adrenal cortical exhaustion	Doc. TLV 1981
15 000 ppm (42 d)	Evidence of mild stress, physiological adaptation	Doc. TLV 1981
10 000 ppm (22 d)	Mild metabolic stress; serum calcium fell significantly then rose; no apparent physiological effects	Doc. TLV 1981; Gordon 1968
SPECIES: Guinea Pig		
150 000 ppm (up to 73 d)	Higher calcium and lower phosphorus levels maintained after 20 d of exposure. These changes indicative of parathyroid stimulation	Schaefer et al. 1961. IN NIOSH Crit. 1976
150 000 ppm (2 to 7 d)	Surface tension of lung tissue returns to normal after exposure; reduce pulmonary edema. Hyaline membranes disappear	Schaefer et al. 1964. IN NIOSH Crit. 1976
150 000 ppm (24 h/d for 7 d)	Decreased respiratory acidosis and sympathoadrenal responses by day 3 of exposure	Schaefer et al. 1968. IN NIOSH Crit. 1976
SPECIES: Rat		
30 000 ppm (3 wk)	Edema	Niemoeller and Schaefer 1962. IN NIOSH Crit. 1976

7.4.2 Teratogenicity.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Rabbit		
100 000 to 130 000 ppm (4-10 h/2-3 d)	(7 to 12 d pregnant) Cardiac malformations in newborns	Grote 1965. IN NIOSH Crit. 1976
100 000 ppm	(7-12 d pregnant) Teratogenic effects	RTECS 1979
SPECIES: Rat		
60 000 ppm (24 h)	TC_{LO} (10 d pregnant) Teratogenic effects	GE 1979
60 000 ppm (24 h)	(10 d pregnant) Teratogenic effects	RTECS 1979
60 000 ppm (24 h)	Cardiac malformations in newborns (5 to 21 d pregnant)	Haring 1960. IN NIOSH Crit. 1976

7.4.3 Carcinogenicity.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Mouse		
CO_2 snow (solid CO_2) (240 d)	Administered as a chronic irritant. Author concluded that chronic application of a nonspecific cold irritant for at least 240 d resulted in carcinoma development in mice	Mansens 1931. IN NIOSH Crit. 1976

7.5 Symptoms of Exposure

General symptoms of exposure found in most information sources have not been specifically referenced. Only those of a more specific or unusual nature have their sources indicated.

7.5.1 Inhalation.

1. Mild narcotic effects.
2. Stimulation of the respiratory centre.

3. Stinging sensation in eyes, nose and throat at high concentrations.
4. Increased blood pressure and pulse.
5. Headache and dyspnea on mild exertion.
6. Acidosis and adrenal cortical exhaustion with prolonged continuous exposure.
7. Unconsciousness due to asphyxiation.
8. Death.

7.5.2 Eye Contact. Solid carbon dioxide causes severe burns (NIOSH Crit. 1976).

7.5.3 Skin Contact.

1. Carbon dioxide at room temperature will not injure the skin (NIOSH/OSHA 1981).
2. Contact of carbon dioxide snow or solid with the skin may cause frostbite (Matheson 1980).

7.6 Normal Atmospheric Levels of Carbon Dioxide

Typical air may have 320 ppm (0.032 percent) CO_2. This may vary for a number of circumstances. For example, a theatre full of people could have 2500 ppm (0.25 percent) CO_2 (NIOSH Crit. 1976). The variance of atmospheric CO_2 on one sea cruise was 200 to 700 ppm (Kelley 1971). The levels above active soil in the absence of wind could be 1500 ppm (Kelley 1973). A brewery cellar had levels measured at 1.08 percent (10 800 ppm). A number of deaths by asphyxiation have been reported in ship holds and other confined space - especially those where CO_2 is produced by combustion (e.g., engines) or by decomposition (e.g., silos). Holds of a number of fishing vessels were measured for CO_2 and valves from 1 to 4 percent were measured. Carbon dioxide levels were also measured in silos yielding results such as 78 percent CO_2 0.3 m above the fill, 17 percent CO_2 with good ventilation, and 30 to 40 percent CO_2 above the fill after closing (NIOSH Crit. 1976). These values are presented to give perspective to CO_2 values one might encounter in the absence of a spill.

8 CHEMICAL COMPATIBILITY

8.1 Compatibility of Carbon Dioxide with Other Chemicals and Chemical Groups

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
GENERAL														
Water									•				Forms carbonic acid	Sax 1979
SPECIFIC CHEMICALS														
Acrylaldehyde (Acrolein)	•			•									Can cause polymerization	Bretherick 1979
Aluminum (Powder)		•											Burns in a CO_2 atmosphere if ignited	Bretherick 1979
Aluminum (Powder) and Sodium Peroxide			•										CO_2 gas passed over mixture explodes	NFPA 1978
Aziridine				•									Can catalyze polymerization	Bretherick 1979
Cesium Monoxide (Dicesium Oxide)		•											Burns in a CO_2 atmosphere if ignited, incandescence can occur in presence of moisture	Bretherick 1979; NFPA 1978
Diethyl Magnesium		•											Burns in a CO_2 atmosphere if ignited	NFPA 1978

8.1 Compatibility of Carbon Dioxide with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Lithium		•											Burns in a CO_2 atmosphere if ignited	NFPA 1978
Lithium Acetylene Carbide Diamine		•											Burns on contact with CO_2	NFPA 1978
Magnesium (Powder) and Sodium Peroxide			•										CO_2 gas passed over mixture explodes	NFPA 1978
Potassium			•										Mixture of solid potassium and carbon dioxide explodes when subjected to shock	NFPA 1978
Potassium Acetylide		•											Mixture incandesces when warmed	NFPA 1978
Sodium		•	•										Sodium burns in CO_2 atmosphere if ignited; an explosion can occur if two solid forms are brought together by impact	NFPA 1978
Sodium and Ammonia (Liquid)			•										Forms explosive sodium carbonyl	NFPA 1978
Sodium Carbide		•											Incandesces on contact	NFPA 1978

8.1 Compatibility of Carbon Dioxide with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Sodium Potassium Alloy		•											Will explode with solid CO_2 under slight impact	NFPA 1978
Titanium (Powdered)		•											Burns in a CO_2 atmosphere above 550°C when ignited	NFPA 1978
CHEMICAL GROUPS														
Flammable Materials	•												Release of CO_2 gas may cause electrostatic charges and sparks	Bretherick 1979
Metal Acetylides	•												Many metal acetylides burn on contact with CO_2	Bretherick 1979
Metal Dusts	•	•											Many metal powders or dusts burn in CO_2 atmosphere if ignited	Bretherick 1979
Metal Hydrides and Ethers		•											CO_2 presence in ethers with metal hydrides can cause explosion (e.g., aluminum hydride)	Bretherick 1979

8.1 Compatibility of Carbon Dioxide with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
Metals and Nitrogen	•												Some powdered metals ignite on heating in carbon dioxide and nitrogen mixtures including Be, Ca, Ce, Th, Ti, U, Zr	Bretherick 1979

9 COUNTERMEASURES

9.1 Recommended Handling Procedures

The following procedures have been derived from a literature review. To avoid any deviation from the intended meaning, the wording of the original source has been presented essentially unchanged. In so doing, it is recognized that there may be some discrepancies between different sources of information. It is recognized that countermeasures are dependent on the situation, and thus what may appear to be conflicting information may in fact be correct for different situations. The following procedures should not be considered as Environment Canada's recommendations.

9.1.1 Fire Concerns. Carbon dioxide is a noncombustible material. It is frequently used as a fire extinguishing material. Some materials, notably powdered metals, will remain burning even in a carbon dioxide atmosphere.

9.1.2 Fire Extinguishing Agents. Carbon dioxide is a fire extinguishing agent. Use water spray to cool containers involved in a fire to prevent rupture.

9.1.3 Spill Actions, Cleanup and Treatment. Stop or reduce discharge of material if this can be done without risk. Liquid and solid carbon dioxide must not be allowed to contact the skin because of the hazard of frostburn.

Water spray may be used to convert any form of carbon dioxide to carbonic acid which may then be neutralized with alkalis. If a leak in a container cannot be stopped, remove the leaking container to a safe place in open air and repair the leak or allow the cylinder to empty (NIOSH/OSHA 1981). Gas or liquid from a leaking cylinder or other container may be directed to enter water or a solution of monoethanolamine (MEA). The latter offers an efficient means of CO_2 absorption (Albanese 1979).

9.1.4 Disposal. Carbon dioxide in most amounts can be safely released to the atmosphere given that it is readily mixed before entering populated areas, low areas where it might collect and directly over freshwater lakes and streams (Baes 1980, 1980a).

9.1.5 Protective Measures. For entry into a situation where the spilled material and its characteristics are unknown, self-contained breathing apparatus and a totally encapsulated chemical suit should be worn.

If the spilled material is known to be carbon dioxide:

- Response personnel should be provided with and required to use impervious clothing, gloves, faceshields (20 cm minimum), and other appropriate protective clothing

necessary to prevent the skin from becoming frozen from contact with solid carbon dioxide or from contact with vessels containing carbon dioxide (NIOSH/OSHA 1981).

- Safety glasses are recommended when handling high pressure cylinders (Air Products MSDS 1978).
- Loose-fitting gloves of impermeable material such as leather are recommended when working with cold liquid, solid, or vapours of carbon dioxide (Air Products MSDS 1978).

The following is a list of the minimum respiratory protection recommended for personnel working in areas where carbon dioxide is present (NIOSH/OSHA 1981).

Condition	Minimum Respiratory Protection* Required Above 5000 ppm
Gas Concentration 50 000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
Greater than 50 000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
	A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any escape self-contained breathing apparatus.

* Only NIOSH-approved or MSHA-approved equipment should be used.

9.1.6 Cylinder Storage Precautions. Prevent entrapment of liquid in closed systems. Use only in well-ventilated areas. Compressed gas cylinders contain gaseous and liquid carbon dioxide at extremely high pressure and should be handled with care. Use a pressure-reducing regulator when connecting to lower pressure piping systems. Chain cylinders when in use. Never use direct flame to heat a compressed gas cylinder. Use a check valve to prevent back flow into storage container. Avoid dragging, rolling or sliding cylinders, even for a short distance (Air Products MSDS 1978).

Store liquid containers and cylinders in well ventilated areas. Keep cylinders away from sources of heat. Storage should not be in heavy traffic areas to prevent accidental knocking over or damage from passing or falling objects. Valve caps should remain on cylinders not connected for use. Segregate full and empty cylinders. Storage areas should be free of combustible material. Avoid exposure to areas where salt or other corrosive chemicals are present. Store carbon dioxide cylinders with the valve end up (Air Products MSDS 1978).

Do not store in enclosed or sub-surface areas. Do not put dry ice in a closed container where evolved gas cannot escape (GE 1979).

10 PREVIOUS SPILL EXPERIENCE

This section contains information on previous spill experience which will be useful to readers in understanding spill response and countermeasures. Only those which meet the criteria are included, and thus, the number of experiences is not an indication of the problems or frequency of spillage. As technology in spill control advances, this section will be updated in future manual revisions to include the most useful information.

Although spills of this material have been recorded, no significant information regarding cleanup methods or response has been documented.

11 ANALYTICAL METHODS

The general approach adopted for each of the Priority Chemicals was as follows.

Methods have been documented here for the analysis of samples from air, water and soil in a normally equipped chemical laboratory remote from the spill site. Customary sources of standard or recommended analytical methods were consulted, and outlines are presented for each chemical. These sources included publications of the U.S. National Institute for Occupational Safety and Health (NIOSH), the U.S. Environmental Protection Agency (EPA), the American Water Works Association (AWWA), the American Society for Testing and Materials (ASTM), and the American National Standards Institute (ANSI).

If the standard or recommended methods were judged to be reliable and specific enough for the analysis of environmental and materials samples from spill sites and if they do not require highly specialized laboratory equipment, no additional methods were sought.

If especially simple, reliable tests (e.g., commonly used industrial methods) were found, they have been presented as well.

11.1 Quantitative Method for the Detection of Carbon Dioxide in Air

11.1.1 Gas Chromatography (NIOSH 1977). A range of 2270 to 10 000 ppm of carbon dioxide in air can be determined using gas chromatography. A known volume of air, approximately 3 to 4 L, is collected in a gas sampling bag. There is no sample preparation. A suitable aliquot of the sampled air is injected into a gas chromatograph equipped with a thermal conductivity detector. The sample is injected into a 5 ft. x 1/4 in. stainless steel column packed with 80/100 mesh Porapak QS. The typical gas chromatograph operating conditions are: helium gas flow at 100 mL/min, injector temperature is ambient, detector temperature is 70°C, and the column temperature is also ambient. The carbon dioxide in the aliquot of air sample is determined using the area under the peak and a calibration curve.

11.2 Qualitative Method of the Detection of Carbon Dioxide in Air

11.2.1 Drager Tube (Drager 1979). Carbon dioxide may be determined in air with the use of a carbon dioxide Drager tube which will show a colour change from white to violet on an indicating layer as air is drawn through the tube. The tube is scored at both ends

and broken and the reaction ampoule is activated. The colour change is due to a reaction between carbon dioxide and hydrazine.

11.3 Quantitative Method for the Detection of Carbon Dioxide in Water.

11.3.1 Direct Titration (ASTM 1979). This method is suitable for estimation of free carbon dioxide in water, generally in concentrations greater than 10 ppm.

A minimum volume of 1 L of sample is collected in an appropriate container. A 100 mL volume of sample is placed in a 250 mL beaker and 5 drops of phenolphthalein indicator are added. The sample is titrated immediately with 0.04 N sodium hydroxide solution until the first faint pink colour, or use a pH meter to titrate to a pH of 8.3. The free carbon dioxide is determined from the aliquot of base used.

11.4 Qualitative Method for the Detection of Carbon Dioxide in Water

The sample is collected as in Section 11.3.1. Carbon dioxide in water will form a white precipitate of barium carbonate when reacted with a solution of 0.2 M barium hydroxide (Welcher 1955).

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EnviroTIPS

Common Abbreviations

BOD	biological oxygen demand
b.p.	boiling point
CC	closed cup
cm	centimetre
CMD	count median diameter
COD	chemical oxygen demand
conc	concentration
c.t.	critical temperature
eV	electron volt
g	gram
ha	hectare
Hg	mercury
IDLH	immediately dangerous to life and health
Imp. gal.	imperial gallon
in.	inch
J	joule
kg	kilogram
kJ	kilojoule
km	kilometre
kPa	kilopascal
kt	kilotonne
L	litre
lb.	pound
LC_{50}	lethal concentration fifty
LC_{LO}	lethal concentration low
LD_{50}	lethal dose fifty
LD_{LO}	lethal dose low
LEL	lower explosive limit
LFL	lower flammability limit
m	metre
m	meta
M	molar
MAC	maximum acceptable concentration
max	maximum
mg	milligram
MIC	maximum immission concentration
min	minute or minimum
mm	millimetre
µg	microgram
µm	micrometre
°Be	degrees Baumé (density)
MMAD	mass median aerodynamic diameter
MMD	mass median diameter
m.p.	melting point
MW	molecular weight
N	newton
NAS	National Academy of Sciences
NFPA	National Fire Protection Association
NIOSH	National Institute for Occupational Safety and Health
nm	nanometre
o	ortho
OC	open cup
p	para
P_c	critical pressure
PEL	permissible exposure level
pH	measure of acidity/alkalinity
ppb	parts per billion
ppm	parts per million
P_s	standard pressure
psi	pounds per square inch
s	second
STEL	short-term exposure limit
STIL	short-term inhalation limit
T_c	critical temperature
TC_{LO}	toxic concentration low
Td	decomposition temperature
TD_{LO}	toxic dose low
TL_m	median tolerance limit
TLV	Threshold Limit Value
Ts	standard temperature
TWA	time weighted average
UEL	upper explosive limit
UFL	upper flammability limit
VMD	volume mean diameter
v/v	volume per volume
w/w	weight per weight